INTERMOLECULAR POTENTIAL ENERGY FUNCTIONS FOR PAIRS OF SIMPLE POLYATOMIC MOLECULES AND THEIR APPLICATION TO PROPERTIES OF GASES AND LIQUIDS

By

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PREFACE

There have been several attempts to calculate potential energy functions for relatively small polyatomic molecules in order to determine the proper form of these potentials. The end result of these calculations has usually been the correlation of properties of these polyatomic molecules using the calculated form of the potential energy function as the basis. These calculations, therefore, have been more qualitative than quantitative in their application.

In the present work these calculated potential energy functions are tested in a more quantitative manner. In Part I interaction parameters for constituent atoms of polyatomic molecules are determined from inert gas and diatomic gas data, and are then used in the calculation of potential energy functions for the more complex polyatomic molecules considered. These calculated potential energy functions are then tested by calculating second virial coefficients and comparing with experimental data.

Most of the results of calculated potential energy functions in previous works have been applied to the gas state. In Part II of the present work an attempt is made to determine if the calculated potential energy functions of Part I can be applied to the properties of pure liquids. Because of the complexity of using elaborate liquid models, the present work makes use of a simplified model of the liquid state, the smoothed potential cell model. Experimental measurements of

the thermal pressure coefficient for three compounds are presented and the molar volume, thermal pressure coefficient and configurational energy-volume relationships are discussed in light of the predictions of this model. Also included in Part II is an investigation of the configurational energy-volume relationship in liquids using the radial distribution function as the basis for discussion.

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CHAPTER I

INTRODUCTION AND REVIEW

When considering the physical properties of pure liquids and gases one soon finds that in order to understand the observed properties, it is necessary to have some understanding of interactions on the molecular scale. The simplest system in which interactions between atoms and molecules can be described is one which consists of an isolated pair of atoms (or molecules). From quantum mechanical derivations, it has been determined that a pair of atoms will attract each other at relatively large separations and will repel each other at very small separations. At some intermediate point there will be no net force of interaction. These interactions are described by the mutual pair potential energy as a function of interatomic separation. The force acting on each particle of the isolated pair at any given separation is determined as the negative of the slope of their potential energy function at that separation. The exact form of the potential energy function cannot in general be derived from quantum mechanics because of the complexity of the problem. For this reason several attempts have been made to determine a mathematically simple approximation to the potential energy function which would at least approach physical reality.

Potential Energy Functions for Simple Centers of Interaction

The most widely used of these approximations has been the

Lennard-Jones potential and this will be the only single-[illegible] tial energy function discussed here. This and other forms of [illegible] energy functions for single centers of interaction are discussed by Hirschfelder, Curtiss, and Bird (1).

The Lennard-Jones 6-12 potential has been found to be useful in the correlation of properties of the inert gases (atoms) and other gases with relatively small molecules. This potential energy function is not necessarily the best representation for each one of this type of molecule, but it does serve quite well for many. This potential for non-polar molecules is

$$U(r) = \mathcal{E}^* \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^{6} \right] = 4 \mathcal{E}^* \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^{6} \right] \qquad (1)$$

The meanings of the symbols can be seen in Figure 1 and are described below.

$U(r)$ = Potential energy of interaction

r_m = Value of r at the minimum of $U(r)$

$\mathcal{E}^*$ = Value of $-U(r)$ at the minimum of $U(r)$

r_0 = Value of r when $U(r) = 0$

r = Distance between centers of atoms or molecules

The term which contains the sixth-power exponent represents the long-range attractive forces and is predicted to be as by quantum mechanics for nonpolar molecules. The term containing the twelfth-power exponent represents the short-range repulsive forces. This form of representation of the repulsive forces was not predicted by quantum mechanics. The twelfth power is chosen somewhat arbitrarily for mathematical convenience and because the repulsive forces are known to be very large and to change rapidly at small separations.

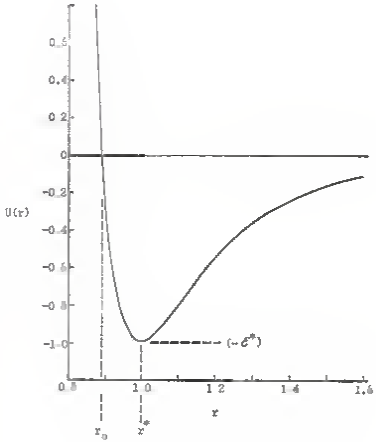

Figure 1 Lennard-Jones 6-12 Potential

Interactions [illegible] molecules

For a more [illegible] the exponents "6" and "12" do not appear to be [illegible]. For this reason it is desirable to generalize this form of the potential energy function to allow other values to the exponents. When this is done, one gets an equation of the form

$$U(r) = \frac{\mathcal{E}^*}{1-\frac{m}{n}}\left[\frac{m}{n}\left(\frac{r^*}{r}\right)^n - \left(\frac{r^*}{r}\right)^m\right] \qquad (2)$$

where m = Attractive exponent

n = Repulsive exponent, n>m

r = Distance between molecular centers

r^*, $\mathcal{E}^*$ are defined as before

The parameter r_0 is given in terms of r^* by

$$r_0^3 = r^{*3}\left(\frac{m}{n}\right)^{\frac{3}{n-m}} \qquad (3)$$

Appendix B contains several of these n-m potentials in tabular form.

There have been several attempts to determine the proper form of the function representing the potential energy of interaction of two isolated polyatomic molecules as a function of the distance between their centers. Since these previous works influenced and were used in the present work, a brief summary of them will be given here. These previous papers are discussed by Prigogine (2).

Mayer and Lambert (3). These authors assumed that the potential energy of interaction between two spherically symmetrical polyatomic molecules could be found by summing the interactions between all possible pairs of atoms in the two molecules and averaging these interactions over all orientations. It was assumed that there was un-correlated

free rotation of the molecules. The interactions between [illegible] atoms on adjacent molecules were assumed to follow the Lennard-Jones 6-12 potential energy function.

The procedure of calculation was as follows: an expression was written for the energy of interaction between every pair of atoms (one from each molecule) in two interacting molecules as a function of orientation and distance between molecular centers. This expression was then averaged over all orientations of the two molecules, giving equal weight to all orientations. The total mutual molecular pair potential energy was equal to the sum of the interaction energies for the atom pairs.

The integrations in the averaging process were done in closed form, which made the results easier to use than the infinite series solutions by Atoji and Lipscomb (4) which will be discussed later.

Although the results were applicable to any two molecules of the type A_aB_b and C_cD_d, Hamann and Lambert made calculations for only one case. The assumptions used were that:

1. $A = C$, $B = D$, $a = c = 1$, $b = d = 4$; then the interactions between molecules of the same kind, AB_4,

2. the size of all atoms in the molecules is the same; i.e. $r^* = r_A^* = r_B^*$,

3. the minimum in the potential energy function for all pairs of atoms is the same and equals $-\epsilon^*$,

4. $r^* = 2\rho_i$, where ρ_i is the distance from the center of the molecule to the center of the peripheral atoms.

When the potential energy function (a function of distance between molecular centers) was calculated for this case, it was found that a

[illegible] an empirical fit to the result could be obtained using the Lennard-Jones type of potential energy function (Equation 2) with exponents m = 7 and n = 28, i.e., a 7-28 potential energy function. The constants determined parameters for this potential energy function for several molecules from second virial coefficient data. This potential was found to correlate gas data for molecules such as CF_4, SiF_4, SF_6 and $C(CH_3)_4$ very well, and was found to give size parameters for these molecules which were more reasonable than those from the Lennard-Jones 6-12 potential.

Since their results for interactions between two molecules are given correctly and will be needed later, their general equations will be given here. The following equations apply to interactions between two molecules A_aB_b and C_cD_d, assuming only that there is un-correlated, free rotation and that the total interaction energy is the sum of all interactions between atom pairs. Equal weight is given to all orientations of the two molecules. No other assumptions were used.

$$U(R) = u_{AC} + u_{AD} + u_{BC} + u_{BD} \qquad (4)$$

where U(R) = Total interaction potential energy between the two molecules

R = Distance between molecular centers

u_{AC} = Potential energy of interaction between central atoms (atoms A and C are at center of molecule)

u_{AD} u_{BC} = Potential energy of interaction between central and all peripheral atoms

u_{BD} = Potential energy of interaction between all peripheral atoms

$$u_{AC} = \text{etc}\,\mathcal{E}^{*}_{AC}\left[\left(\frac{r^{*}_{AC}}{R}\right)^{12} - 2\left(\frac{r^{*}_{AC}}{R}\right)^{6}\right] \tag{5}$$

$$u_{AD} = \tfrac{1}{2}\text{etc}\,\mathcal{E}^{*}_{AD}\left\{\frac{\left(r^{*}_{AD}\right)^{12}}{10R^{10}\rho_{CD}}\left[\left(1-\frac{\rho_{CD}}{R}\right)^{-10} - \left(1+\frac{\rho_{CD}}{R}\right)^{-10}\right]\right.$$

$$\left. - \frac{\left(r^{*}_{AD}\right)^{6}}{2R^{5}\rho_{CD}}\left[\left(1-\frac{\rho_{CD}}{R}\right)^{-4} - \left(1+\frac{\rho_{CD}}{R}\right)^{-4}\right]\right\} \tag{6}$$

$$u_{BC} = \tfrac{1}{2}\text{etc}\,\mathcal{E}^{*}_{BC}\left\{\frac{\left(r^{*}_{BC}\right)^{12}}{10R^{10}\rho_{AB}}\left[\left(1-\frac{\rho_{AB}}{R}\right)^{-10} - \left(1+\frac{\rho_{AB}}{R}\right)^{-10}\right]\right.$$

$$\left. - \frac{\left(r^{*}_{BC}\right)^{6}}{2R^{5}\rho_{AB}}\left[\left(1-\frac{\rho_{AB}}{R}\right)^{-4} - \left(1+\frac{\rho_{AB}}{R}\right)^{-4}\right]\right\} \tag{7}$$

$$u_{BD} = \tfrac{1}{2}\text{etc}\,\mathcal{E}^{*}_{BD}\left\{\frac{\left(r^{*}_{BD}\right)^{12}}{5\rho_{AB}^{10}\rho_{CD}R}\left[\frac{\gamma}{\beta^{5}} - \frac{\gamma}{\alpha^{5}} + \frac{40\gamma^{3}}{3\beta^{6}} - \frac{40\gamma^{3}}{3\alpha^{6}} + \frac{48\gamma^{5}}{\beta^{7}} - \frac{48\gamma^{5}}{\alpha^{7}}\right.\right.$$

$$\left. + \frac{64\gamma^{7}}{\beta^{8}} - \frac{64\gamma^{7}}{\alpha^{8}} + \frac{256\gamma^{9}}{9\beta^{9}} - \frac{256\gamma^{9}}{9\alpha^{9}}\right]$$

$$\left. - \frac{2\left(r^{*}_{BD}\right)^{6}}{\rho_{AB}^{2}\rho_{CD}R}\left[\frac{\gamma}{2\beta^{2}} - \frac{\gamma}{2\alpha^{2}} + \frac{2\gamma^{3}}{3\beta^{3}} - \frac{2\gamma^{3}}{3\alpha^{3}}\right]\right\} \tag{8}$$

[illegible] (9)

$$[illegible] = \left[1 + \frac{\pi}{\rho_{AB}}\right]^2 \sim y^2 \qquad (10)$$

$$[illegible] = \left[1 - \frac{\pi}{\rho_{AB}}\right]^2 \sim y^2 \qquad (11)$$

ρ = Distance from center of [illegible] cms in the same molecule

r^* ϵ^* = Parameters in Lennard-Jones 6-12 potential for atoms

Subscripts A B C D refer to the atoms involved.

Notice that these equations can be used directly for interactions between two isolated CF_4 molecules, where a = c = 1, b = d = 4 and

$$U(R) = u_{CC} + 2u_{CF} + u_{FF} \qquad (4a)$$

The value of ρ_{CF} to use is the C - F bond length. Other molecules of this type include CCl_4, SF_6, SiF_4, $C(CH_3)_4$, and $Si(CH_3)_4$ if CH_3 groups are considered to interact as single centers.

The results of Hennus and Lambert can also be applied to molecules in which there is no atom at the center, such as in the diatomic gases H_2, N_2, O_2, F_2, and Cl_2. For these molecules, Equation 8 gives the total interaction. The parameters for these molecules are a = c = 0, b = d = 2, and the value of ρ in each case is one-half the bond length in each of the molecules.

There is another type of molecule for which the equations of Hennus and Lambert can be used. These are molecules such as C_2F_6 and $C_2(CH_3)_6$ in which, when freely rotating, the constituent atoms are always found in two concentric spheres. Equation 8 can be used for all

[illegible] tween these molecules. For example, when calcu- [illegible] erated pair potential energy function of C_2F_6, the total interaction is given by Equation 4, in which each of these values of u is determined by use of Equations 3 only. Equations 5, 6, and 7 contribute nothing to the total potential energy for this type of molecule which has no atom at its center. If it is desirable to calculate interactions between molecules in which there are more than two spherical shells of atoms when the molecule is rotated freely, Equation 8 may be applied to the interactions among atoms in each pair of these shells. One must be careful, however, that all interactions are considered. The values of ρ to be used in such case are the distances from the center of the molecule to the atoms involved.

Atalj and Lingenuth (4). Atalj and Lingenuth also assumed that the centers of interaction between two polyatomic molecules are in the constituent atoms rather than at the center of the molecule. They assumed that there was no correlated free rotation of all molecules and that the total mutual potential energy of interaction between a pair of isolated molecules could be determined as the sum of interactions of all pairs of constituent atoms averaged with equal weight over all orientations of the two molecules. In order to make calculations, the authors assumed that the constituent atoms interact according to the Lennard-Jones 6-12 potential energy function. Thus, their results should be equivalent to those of Nemano and Lambert since the assumptions are the same. This was shown to be true, even though the integrations were performed by a different method from that of Nemano and Lambert to give infinite series solutions.

Calculations of the minimum in the [illegible] of CF_4, CCl_4 and SF_6 were made by analogous interaction [illegible] of fluorine atoms and using the derived equations for the parameters for fluorine atoms in CF_4 and SF_6, these authors used parameters ($\mathcal{E}^*$ and r^*) determined from data on gas viscosity of F_2. They used these same parameters for carbon and for sulfur atoms also. In the calculations for CCl_4 the parameters for the chlorine atoms were determined from data on the second virial coefficient of Cl_2 gas. The parameters for the carbon atoms were taken to be those of neon. These calculated values of $\mathcal{E}^*$ and r^* for the molecules were compared with 6-12 potential energy function parameters determined from experimental data and were found to be in reasonable agreement. No mention was made of the shapes of the calculated potential energy functions. It will be shown later that a comparison of $\mathcal{E}^*$ and r^* values without taking the shape of the potential energy function into account is of doubtful value.

Halasz (2,5) Halasz derived by use of Gegenbauer polynomials the general expression for the interaction of an isolated pair of spherically symmetrical polyatomic molecules. He considered the centers of interaction to be in the constituent atoms, and since the largest interactions are between peripheral atoms he considered the entire interaction between molecules to be due to interactions among peripheral atoms. He assumed that interactions between pairs of atoms could be represented by a Lennard-Jones 6-12 potential energy function and that the total interaction between molecules is the sum of the interactions between all pairs of atoms. His derivation is valid for two molecules in a given position and does not attempt to give the average interaction over all orientations of the two molecules as is the

papers discussed previously. In his general expression there are central terms (terms which do not depend upon molecular shape, structure, and orientation) and non-central terms which depend upon the shape, structure and orientation of the molecules. Since these non-central terms determine the orientation effects for polyatomic molecules these terms were of the greatest interest. The author concluded that for symmetrical polyatomic molecules the non-central terms make only a small contribution as long as the separation between molecules is large compared to the size of the molecule. The central terms were found, in general, to agree with treatments which assumed free rotation of the molecules to get average potentials. From the data on the second virial coefficient of CF_4 and the central terms of his derivation, he determined that the Lennard-Jones 6-12 potential interaction parameters for the fluorine atom should be

$$r_F^* = r_{Ne}^*$$

$$\mathcal{E}_F^* = \frac{1}{2}\,\mathcal{E}_{Ne}^*$$

For CCl_4 he also found that $\mathcal{E}_{Cl}^* \pm \mathcal{E}_A^*$

This indicates that when calculating interactions between peripheral atoms in molecules, the r^* values for the noble gas of similar size can probably be used for peripheral atoms but some care must be exercised in the choice of the $\mathcal{E}^*$ values used.

Dacey and Vanderslice (6). One of the most direct methods for determining potential energy functions of gases is the scattering of ions in gases. These experiments usually yield the potential energy of interaction over very narrow ranges of separations however. For this reason these results, at the present time, are of limited value in

[redacted]ort o s of the potential energy functions to [redacted] properties It is hoped that this will not be true [redacted] Lee Year Future. The paper by Cisney and Vanderslice covers a narrow range of molecular separations, but some of their calculations are similar to the work done here and should be mentioned.

From ion scattering data potential energy functions were determined for the systems $N^+ - CH_4$, $N^+ - C_2H_6$, $N_2^+ - CH_4$, $N_2^+ - C_2H_6$, $N^+ - CF_4$, $N^+ - C_2F_6$, $N_2^+ - CF_4$, and $N_2^+ - C_2F_6$. These potential energy functions were valid at separations where the forces were repulsive. The authors used the potential energy functions for CH_4 and CF_4 with the hydrogen ions to predict potential energy functions for hydrogen ions and C_2H_6 and C_2F_6.

In the first scheme, the interactions between $N^+ - C_2H_6$ and $N^+ - C_2F_6$ were assumed to be due entirely to interactions between hydrogen ions and the peripheral hydrogen and fluorine atoms in C_2H_6 and C_2F_6 respectively. The interaction centers at the peripheral hydrogen and fluorine atoms were assumed to be at the centers of these atoms. The same assumptions were made for interactions between $N^+ - CH_4$ and $N^+ - CF_4$ and interaction parameters for hydrogen and fluorine atoms with N^+ were evaluated from the $H^+ - CH_4$ and $H^+ - CF_4$ data. This was done by deriving equations for the interaction of an atom with a freely rotating polyatomic molecule as in the papers discussed previously. These parameters for hydrogen and fluorine determined from CH_4 and CF_4 data were then used to calculate the potential energy of interaction between $N^+ - C_2H_6$ and $N^+ - C_2F_6$. The calculated and experimental results agreed within a factor of two over the entire range of measurements. A similar procedure was followed to calculate the potential energy functions for

$H_2^+ - C_2H_6$ and $H_2^+ - C_2F_6$ fr[illegible] for $H_2^+ - C$[illegible] and $H_2^+ - CF_4$. In this case [illegible] two centers of interaction and the calcul[illegible]. The agreement again was within a factor of two.

The other scheme used was to assume that in C_2H_6 and C_2F_6 there were two centers of interaction. For example ethane was considered to be two methane molecules separated by the normal C - C distance in ethane. A similar assumption was made for C_2F_6. The interaction centers were taken at the center of the carbon atoms in C_2H_6 and C_2F_6. Parameters for CH_3 and CF_3 groups were determined as before from data on CH_4 and CF_4 and the potential energy functions for C_2F_6 and C_2H_6 were calculated. The agreement again was within a factor of two between calculated and experimental potential energies.

CHAPTER II

THE SECOND VIRIAL COEFFICIENT AND POTENTIAL ENERGY FUNCTIONS

The equation of state for imperfect gases can be written in the form

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \cdots \qquad (12)$$

where P = Absolute pressure

V = Volume per mole

T = Absolute temperature

R = Gas constant

The coefficients B(T), C(T), and D(T) are called the second, third, and fourth virial coefficients, respectively, and are directly related to the interactions between the molecules of the gas.

This equation of state diverges at the density of the liquid and is used primarily for gases at low to medium density. The coefficient B(T) is introduced to account for interactions of pairs of molecules, C(T) for interactions between three molecules, D(T) for interactions between four molecules, etc. Therefore, at low density, use of the second virial coefficient is usually sufficient, but as the density increases, other virial coefficients must also be used.

There is a large volume of data available on the second virial coefficient of gases, but data on the third and higher virial coefficients are not so plentiful or so reliable because of experimental

[illegible] accurate data. The [illegible] relatively easily from the second [illegible] virial coefficients. For these reasons further discussion has been limited to the second virial coefficient.

For angle-independent potential energy functions the second virial coefficient is given by (1,7)

$$B(T) = -2\pi N \int_0^\infty \left[e^{-U(r)/kT} - 1 \right] r^2 dr \qquad (13)$$

where the symbols have the same meaning as given previously.

Generalized Lennard-Jones Potential

For the general form of the Lennard-Jones potential energy function Equation 2, the second virial coefficient is given by Hirschfelder Curtiss, and Bird (1)

$$B(T) = \frac{-2\pi N}{3}\left(\frac{s}{c}\right)^{\frac{3}{n-m}} y^{\frac{3}{n-m}} \sum_{j=m}^{n} b^{(j)}(m,n) y^j \qquad (14)$$

where $b^{(j)}(m,n) = \frac{3}{j!\,n}\Gamma\left(\frac{jn-3}{n}\right)$ (15)

$$y = \left(\frac{\epsilon}{kT}\right)\left(\frac{d^n}{s}\right)^{m/n} \qquad (16)$$

$$c = \frac{\epsilon^* (r^*)^m}{1 - m/n} \qquad (17)$$

$$\frac{\quad}{\quad} \tag{18}$$

By simple manipulation, it can be shown that

$$r_0^3 = \left[\frac{A}{C}\right]^{\frac{3}{n-m}} \tag{19}$$

Even for simple polyatomic molecules, the centers of interaction will differ from one another both in location and in magnitude, and if the potential energy functions were empirically fitted by the generalized Lennard-Jones potential, then different molecules would have different values of m and n. It is shown in Equation 14 that the second virial coefficient is a function of m and n as well as of temperature. Calculations of the second virial coefficient were made by hand in the present work for several values of m and n in order to determine how sensitive a function the second virial coefficient is of m and n. For convenience and to make the results more useful the calculations were done in reduced form. The reduced second virial coefficient $B^*(T^*)$ is defined as

$$B^*(T^*) = \frac{B(T)}{\frac{2}{3}\pi N r_0^3} \tag{20}$$

and the reduced temperature T^* is defined as

$$T^* = \frac{kT}{\epsilon} \tag{21}$$

where k = Boltzmann's constant.

Calculations of B^* as a function of T^* have been made for the 6-12 potential energy function and are given by Hirschfelder, Curtiss and

Hird ([illegible] of B^* as a function of T^* for a 7-28 potential [illegible] and Lenhard [illegible] calculations were made for the 6-12 and 7-14 and 7-21 potential [illegible] have more B^* vs. T^* curves for comparison. The infinite series in Equation 14 converges rapidly at high values of T^*, but diverges at low T^*. The calculated B^* values are limited for low values of T^* because of the number of terms it was necessary to use to get reasonable accuracy in B^* for low T^*.

Since the general equations for $\phi(r)$ for an m-n potential (Equations 14-18) are rather complex, the final equations for calculating B^* are given below for each of the potential energy functions mentioned above.

6-12 Potential

$$r_0^3 = 2^{-1/2} r^{*3}$$

$$B^* = -\sum_{j=0}^{\infty} \frac{2^{j+1/2}}{4!} \left[\Gamma\left(\frac{2j-1}{4}\right) \right] (T^*)^{-\frac{2j-1}{4}} \qquad (22)$$

6-15 Potential

$$r_0^3 = 3^{-1/2} r^{*3}$$

$$B^* = y^{1/2} \left[\Gamma\left(\frac{5}{6}\right) - \frac{1}{6} \sum_{j=1}^{\infty} \left[\Gamma\left(\frac{2j-1}{6}\right) \right] \frac{y^j}{j!} \right] \qquad (23)$$

$$y = 3(2)^{-2/3} (T^*)^{-2/3}$$

6-24 Potential

$$r_0^3 = 4^{-1/6}\, r^{*3}$$

$$B^* = y^{1/6}\left[\Gamma\left(\frac{1}{8}\right) - \frac{1}{8}\sum_{j=1}^{\infty}\left[\Gamma\left(\frac{24j-1}{8}\right)\frac{y^j}{j!}\right]\right] \qquad (24)$$

$$y = 4(3)^{-3/4}\,(\pi^*)^{-3/4}$$

7-28 Potential

$$r_0^3 = 4^{-1/7}\, r^{*3}$$

$$B^* = y^{1/7}\left[\Gamma\left(\frac{25}{28}\right) - \frac{3}{28}\sum_{j=1}^{\infty}\left[\Gamma\left(\frac{7j-3}{28}\right)\right]\frac{y^j}{j!}\right] \qquad (25)$$

$$y = 4(2)^{-3/4}\,(\pi^*)^{-3/4}$$

7-21 Potential

$$r_0^3 = 3^{3/14}\, r^{*3}$$

$$B^* = y^{3/14}\left[\Gamma\left(\frac{6}{7}\right) - \frac{1}{7}\sum_{j=1}^{\infty}\left[\Gamma\left(\frac{7-3}{21}\right)\right]\frac{y^j}{j!}\right] \qquad (26)$$

$$y = 3\,2)^{-2/3}\,(\pi^*)^{-2/3}$$

7-12 Potential

$$\epsilon_0^* = 2^{-3/7}\, r_0^{*3}$$

$$B^* = \pi^{3/7}\left[\Gamma\left(\frac{-}{}\right) - \frac{}{14}\sum_{i=1}^{}\left[\Gamma\left(\frac{}{}\right)\right]\right] \qquad (27)$$

$$y = 2(T^*)^{-1/2}$$

The results of these hand calculations are given in Table [illegible] along with values for the 6-12 and 7-28 potentials taken from the sources mentioned above. They are also shown in Figure 2.

The second virial coefficient is not a very sensitive test of the form of the potential energy function because experimental data can often be correlated equally well by several m-n potentials. The values of the parameters ϵ^* and r_0^*, of course, depend upon the potential to which the data was fitted. Therefore it is of interest to examine the relationship among the ϵ^* and r_0^* values for various m-n potentials. It is of especial interest to examine the ϵ^* values since they are more sensitive to changes in potential energy function than r_0^* values.

The relationship among ϵ^* values determined from experimental second virial coefficient data for various m-n potentials can be determined by examination of the Boyle point for m-n potentials. The Boyle temperature, T_B, is defined as the temperature at which the second virial coefficient is zero. Note that when $B(T) = 0$ then $B^*(T^*)$ is also zero. From the reduced second virial coefficient plots given in Figure 2, one can determine the reduced Boyle temperature for each of the potentials used. This was done for the potentials shown in

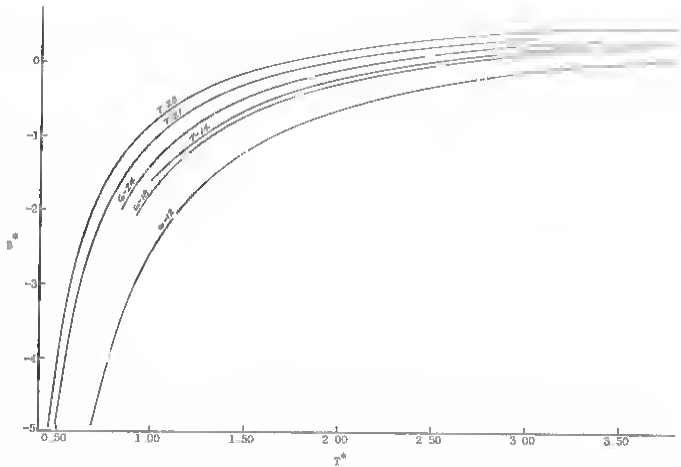

Figure 2. Reduced Second Virial Coefficients for n-n Potentials

Figure 2, and the reduced Boyle temperatures are given in Table 2. The values for the 6-∞ and 7-∞ potentials were given by Monsoo and Lambert (5). These results are also given in Figure 3, which can be used to determine Boyle temperatures for other m-n potentials.

Having these reduced Boyle temperatures makes it possible to determine the relationship among the ϵ^* values for the various m-n potential energy functions determined from experimental data fitted around the Boyle point. At the Boyle point

$$\frac{\epsilon^*_{m-n}}{\epsilon^*_{6-12}} = \frac{T^*_{B\ 6-12}}{T^*_{B\ m-n}} \qquad (28)$$

This ratio is also given in Table 2 for the various potentials. The data in Table 2 show that for a given set of experimental second virial coefficient data in the neighborhood of the Boyle point, the value of ϵ^* for a 7-28 fit to the data would be about twice that for a 6-12 fit. This demonstrates why it is important to specify the shape of the potential energy function when comparing ϵ^* values (also r^* values since ϵ^* and r^* are not independent).

Monsoo and Lambert (5) have empirically evaluated ϵ^* and r^* from second virial coefficients around the Boyle point for several simple molecules for both the 6-12 and 7-28 potentials. These data should afford a check on the value of the ratio $\epsilon^*_{7-28}/\epsilon^*_{6-12}$ determined above. The data, along with this ratio of ϵ^*'s are given in Table 3. It can be seen that, except for the last three molecules the agreement with the value $\epsilon^*_{7-28}/\epsilon^*_{6-12} = 2.07$ obtained from the reduced second virial coefficients is quite good.

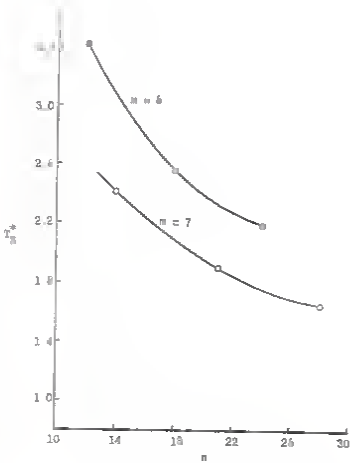

Figure 3 Reduced Boyle Temperatures for m-n Potential Energy Functions

[illegible] -2n potentia[illegible]
[illegible] constant,
[illegible] for those the
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about 0

Fro[illegible] of the second [illegible] calcu-
lated fr[illegible] fferent potentials [illegible] for
whic[illegible] although the data may be empirically fitted to several potential
energy functions equally well the parameters obtained will be quite
different for the different potentials Therefore, one should exercise
care in choosing the potential energy function to which experimental
second virial coefficient data will be fitted especially if the parame-
ters are to be used to calculate other properties

Spherical Shell Model

One of the limitations upon using an n-m type potential energy
function to fit data on polyatomic gases is that in general such a
function does not fit a calculated potential energy function over the
entire range of separations of interest and tables of second virial
coefficients are not available for many different n-m potentials Like-
wise, correlations of second virial coefficients using n-m type poten-
tial energy functions are not easily made over wide ranges of tempera-
ture with the second virial coefficient tables now available

A recent paper by de Boer and Hoover (8) is quite useful as a
step in removing this limitation They have derived equations for the
second virial coefficient based on the spherical shell model and cal-
culated extensive tables by the use of an electronic computer which
can be used in correlating experimental data The spherical shell

[illegible] cules [illegible] may always be found as the [illegible] single [illegible] orientations are given equal [illegible] total interaction [illegible] atoms of two such molecules [illegible] by the [illegible] spherical surfaces which have [illegible] [illegible] This interaction [illegible] that this potential [illegible] exactly [illegible] interaction [illegible] in gases N_2, O_2, F_2, and Cl_2, but not CF_4 since all [illegible] must be in a single spherical shell for this model to apply. [illegible] exactly the same case as covered by Equation 8 [illegible] that this [illegible] be used to [illegible] spherical shell potentials. [illegible] the parameter which determines the shape [illegible] the ratio r^{o}/ρ. When $r^{o}/\rho = \infty$ the Lennard-Jones 6-12 potential results. As r^{o}/ρ decreases, the [illegible] in the potential energy function [illegible] when the potential energy function is plotted on reduced coordinates. Thus with this model there are three adjustable parameters that can be used to fit experimental data: r^{o}, $\mathcal{E}^{o}$ and the parameter for the shape of the potential, r_o^{*}. The parameter r_o^{*} is defined by de Rocco and Hoover as

$$r_o^{*} = \frac{R^{o}}{2\rho} \qquad (29)$$

where R^{o} is the separation at which the minimum occurs in the total potential energy for the isolated pair of molecules. The authors were mainly interested in better correlation of experimental second virial coefficients [illegible] used an electronic computer to calculate the best values of the three adjustable parameters for twenty substances

The parameter r_0^* [illegible] the derivation of the second virial coefficient by [illegible] and Boer, and [illegible] their calculations and in the correlation of experimental data [illegible] as convenient a parameter to use [illegible] the second virial coefficient for a given molecule [illegible] spherical shell model. A more convenient parameter to use [illegible] r^*/ρ [illegible] r^* is the size parameter for the peripheral atom and ρ is the distance from the center of the molecule to the peripheral atoms. [illegible] by calculating several spherical shell potentials one can determine the relationship between r^*/ρ and $R^*/2\rho$. Several spherical shell potentials for different values of r_0^* were calculated in the present work and from these calculations the relationship between R^*/ρ and r^*/ρ was determined. This relationship is given in Table A1 and Figure A1 of Appendix A.

There was another reason for calculating the spherical shell potential for several values of r_0^*. If one calculated a potential energy function for a molecule in which there were interaction centers in positions other than in a single spherical shell, then the spherical shell potential would not fit exactly. In order to determine empirically which spherical shell potential best fits the calculated potential energy function, it is necessary to have these spherical shell potential curves for comparison. Several of these spherical shell potentials were calculated in the present work by electronic computer using Equation 8 and are given in tabular form in Appendix A.

The reduced Boyle temperature as a function of r_0^* given in Table A8 and Figure A2 of Appendix A, for the spherical shell potential was obtained from the second virial coefficients given in the tables of de Rocco and Hoover.

[illegible] a difference [illegible] the spherical shell potential to [illegible] as much between the T-21 potential and $r_o^* = 1.90$ [illegible] identical [illegible]. This is shown by the comparison of [illegible] in Figure 4, where $B(2/3\pi N_o^2 \sigma^3)^{-1}$ is plotted [illegible] potentials mentioned above. The solid lines are for [illegible] and the indicated points are for the spherical [illegible]

Empirical Equations for the Second Virial Coefficient

Benedict, Webb, and Rubin (1940). The Benedict equation is a two-parameter modification of the Beattie-Bridgeman equation which is quite useful for calculating second virial coefficients. The second virial coefficient from this equation is

$$B(T) = \frac{1}{RT}\left[B_o RT - \left(A_o - \frac{C_o}{T^2}\right) - \frac{b_o}{T}\right] \qquad (30)$$

where R = Gas constant

T_c = Critical temperature

P_c = Critical pressure

Pitzer, Lippmann, Curl, Huggins, and Petersen (1955). Pitzer and coworkers correlated properties of [illegible] and their results are based on an empirical acentric factor ω [illegible] to take account of deviations of [illegible] molecules from [illegible] 6-12 potentials. [illegible] which do not fit the 6-12 potential quite well, such as A, Kr, Xe, and CH_4 [illegible] zero. As the molecules become more [illegible] potential the acentric factor

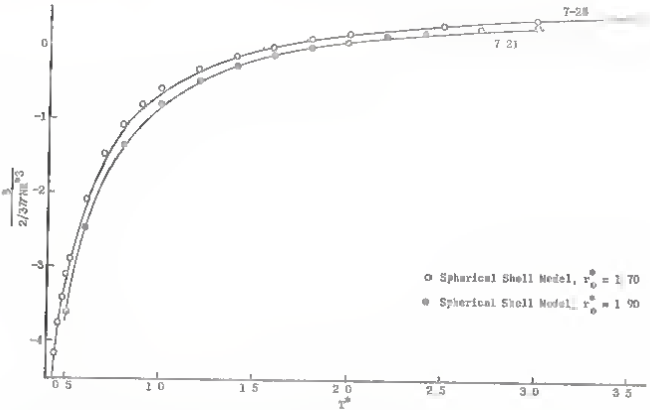


Figure 4 Second Virial Coefficients from m-n Potentials and from the Spherical Shell Potentials

[illegible] pared fr[illegible] pressure for [illegible] [illegible] calculated by Pitzer [illegible] [illegible] given in Table [illegible] [illegible] values [illegible] [illegible] correlatio[illegible]

$$\frac{[illegible]}{T_c} = [illegible] - [illegible] \omega T_r^{-1}$$

$$[illegible] \omega T_r^{-2} - (0.[illegible]) \omega [illegible]$$

$$- 0.0073 \omega T_r^{-3} \qquad (31)$$

[illegible] $T_r = T/T_c$

[illegible]

[illegible] CURVES AND [illegible] ENERGY FUNC[illegible]
PARAMETERS FOR CONSTITUENT ATOMS

[illegible] papers by Hermans and Lambert (3) and by Hoyt and [illegible] functions were derived which can be used to calculate a [illegible] potential energy functions for polyatomic molecules. Hermans and Lambert and [illegible] However used these results to correlate experimental [illegible] coefficients data

[illegible] assigned permanent charges to atoms calculated potential [illegible] and [illegible] a criterion for the calculated [illegible] by [illegible] parameters. They did not [illegible] a [illegible] function into account however [illegible] calculation of potential energy [illegible] to its validity and usefulness [illegible]

[illegible] procedure is further tested [illegible] are used to calculate all [illegible] of [illegible]

[illegible] $\frac{1}{2}$ [illegible] $\frac{1}{2}$ [illegible] $\frac{1}{2}$ [illegible] $\frac{1}{2}$ [illegible] coefficients to [illegible] atoms [illegible] complex molecules [illegible] and [illegible] are very flexible

Notice that if r^* is known for the constituent atoms and ϱ is known for the molecule, then from Equation 8 one can calculate the ratio $U/\mathcal{E}^*$ without knowing $\mathcal{E}^*$. (Recall that U is the total potential energy of interaction and $\mathcal{E}^*$ is the energy parameter for the constituent atoms.) The quantity ϱ is merely one-half the bond distance between atoms in the molecule. The tables of Bowen (11) contain this information and all needed bond lengths are given in Table 4. The size parameters r^*'s, for the atoms in these molecules should not be very much different from those for the nearest inert gas. Therefore, for hydrogen atoms the r^* value chosen will be that for helium; for nitrogen, oxygen and fluorine atoms, r^* will be taken as that for neon; and for chlorine atoms r^* will be taken as that for argon. Parameters for the inert gases for the 6-12 potential are given in Table 5, along with the average values which were used in this work. Using these values of r^* and ϱ, the ratio $U/\mathcal{E}^*$ can be calculated from Equation 8 as a function of the distance between molecular centers R. When $U/\mathcal{E}^*$ is plotted against R, one can locate the minimum in the curve which will have the coordinates $(R^*, -\mathcal{E}^*/\mathcal{E}^*)$, where $-\mathcal{E}^*$ is the minimum value of U. Using the values of the coordinates at the minimum, plots of $U/\mathcal{E}^*$ vs. R/R^* can be prepared. By comparing these reduced potential energy curves with those for m-n potentials (given in Appendix B), one can find an m-n potential which gives a reasonable fit to the calculated potential.

E^*_{6-12} ($\mathcal{E}^*$ for the 6-12 potential) is available for these molecules from experimental gas viscosities and second virial coefficients and can be used to determine E^*_{m-n} by multiplying by the proper factor from Figure 3. That is

(32)

[illegible] $\varepsilon''_m/\varepsilon''$ was calculated previously. One can now calculate directly the 6-12 energy parameter ε'', for the constituent atoms

The r^* and ρ values that were used in these calculations are given in Table 6 along with the r_m^* values for the spherical shell model. The results of the calculations are summarized in Table 7 and the calculated potential energy functions for the molecules are given in reduced form in Tables 8-12 and in Figures 5 and 6. Most of these calculations were done on electronic computers but part of this work was done by hand.

Parameters were actually evaluated only for hydrogen, fluorine, and chlorine atoms, because no further calculations were planned which would require knowledge of nitrogen and oxygen atom parameters. As one would expect, and as shown in Figures 5 and 6, the deviations of the calculated potential energy functions from the 6-12 potential become larger as the size of the molecules increased.

It perhaps seems strange that an m-n potential was approximately related to these calculated potentials when the spherical shell model fits exactly and could give the same results. The reason for using the chosen involving m-n potentials is that these calculations were done and the resulting parameters for hydrogen, fluorine, and chlorine atoms were already used in other calculations when the paper on second virial coefficients for the spherical shell potential was published. In order to assess the accuracy of the original calculations, the parameters for

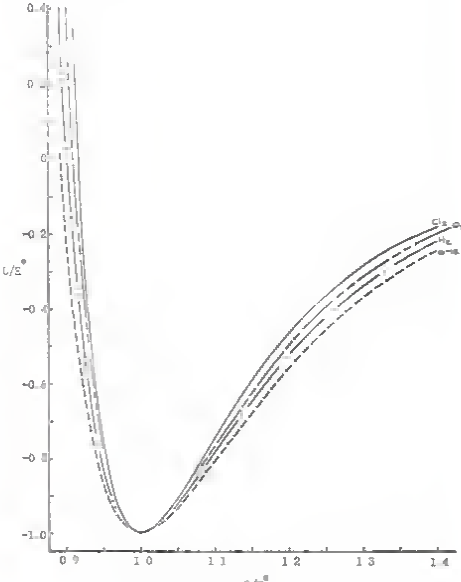


Figure 5 Potential Energy Functions of Diatomic Molecules: N_2, O_2, and Cl_2

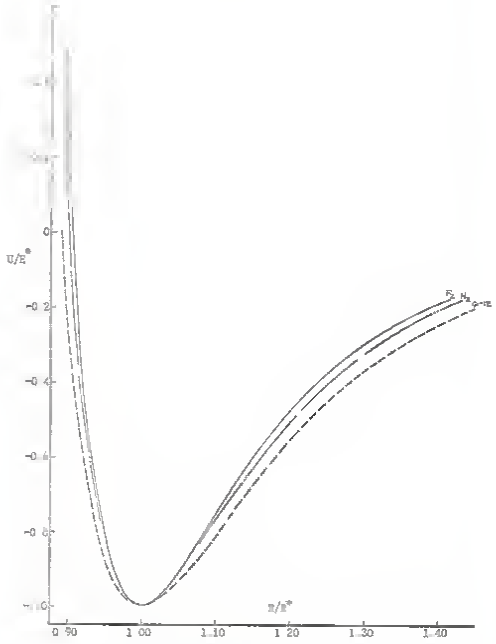


Figure 6 Potential Energy Functions of Diatomic Molecules N_2 and F_2

fluorine and chlorine atoms were re-calculated using the [illegible] potential. From the spherical shell potential, the calculated parameters were

$$(\epsilon^*/k)_F = 93.7^\circ K$$

$$(\epsilon^*/k)_{Cl} = 311^\circ K$$

The energy parameters from the m-n potentials were 90.7°K for the fluorine atom and 303°K for the chlorine atom. This amounts to an error of about 3 percent in the energy parameters caused by approximating the calculated spherical shell potentials with m-n potentials. This error is smaller than the uncertainty in the 6-12 parameters from which they were derived, and were not large enough to warrant repeating the calculations. Therefore later calculations in which these parameters were used were not adjusted.

The values of ϵ^*/k for the constituent atoms were found to be considerably larger than those for the corresponding inert gases as shown in Table 7. This is in contradiction to the findings of Salsburg (5).

If the calculated potential energy function does not differ greatly from the 6-12 potential, the calculated values of B^* should be close to the B^* values for the 6-12 potential determined from experimental data. This can be seen to be true from Table 7 for the diatomic gases. The best way to test the values of B^* calculated for the diatomic molecules is to calculate second virial coefficients using these values of B^*. Since the B^* values used in the above calculations were taken from experimental data, the calculated values of the second virial coefficient will be correct at the Boyle point. If B^* is much in error, however, the calculated values of the second virial coefficient will be considerably different from the experimental values at other temperatures.

because the second virial coefficient is proportional to R^{*3}. These calculations were made and are described separately below for each of the gases. Calculations were not made for H_2 because it would have been necessary to make quantum corrections in the calculations.

Nitrogen (N_2)

There is a considerable volume of experimental second virial coefficient data available for N_2. Experimental measurements were made by Holborn and Otto (13); Michels, Wouters, and de Boer (14); Keyes (15); White, et al. (16); Keesom and van Lammerin (17); and van Itterbeek, et al. (18). These data agree very well, but all points available could not be used because of their number. Enough points were used to show clearly where the second virial coefficient curve is. The data of Michels, et al. and of Holborn and Otto were used to locate the Boyle temperature for N_2, which was found to be 325°K. Since r_0^* for the spherical shell model was found to be 3.29 from Figure A2 the value $T_B^* = 2.72$ is determined. Using these values the value of R^*/k for N_2 is found to be 119 °K. R^* was found to be 3.61 Å when the potential energy function of N_2 was calculated. Thus, the calculated and experimental second virial coefficient curves have been matched at the Boyle point, and any deviations at other temperatures will occur either because the value of R^* is not accurate or the calculated potential energy function does not fit well. The calculated second virial coefficient curve was calculated from the spherical shell potential tables of de Boer and Beaver (5). Values of reduced virial coefficients at various reduced temperatures for $r_0^* = 3.29$ were obtained from a cross-plot of their tables.

Hirschfelder Curtiss and Bird (1) list 6-12 potential parameters based on the data of Holborn and Otto, and Michels et al. The average values of these parameters were used to calculate a second virial coefficient curve for the 6-12 potential, which is plotted in Figure 7

The results of these calculations are shown in Figure 7 It can be seen in this figure that the 6-12 potential fits the data fairly well The curve from the calculated E^* and R^* and the spherical shell potential is not as good but is not badly in error From this plot it appears that the calculated value of R^* is slightly smaller than the one that would give a best fit

Oxygen (O_2)

The second virial coefficient of O_2 has been measured by several experimenters, and these data have been plotted by Myers (19) and by White et al (16) The Boyle temperature was determined from the data of Myers to be 403°K Previously r_e^* was calculated to be 3 07 and from Figure A2 the reduced Boyle temperature is 2 64 From these values E^*/k was determined to be 152 6°K R^* was previously calculated to be 3 70 A Thus, the experimental and calculated second virial coefficients were again matched at the Boyle point The calculated curve from the spherical shell potential and the experimental points are shown in Figure 8 The agreement can be seen to be excellent which indicates that R^* and the shape of the potential energy function are probably nearly correct

Fluorine (F_2)

Experimental measurements of the second virial coefficient of F_2 were made by White et al (16), but their values are probably larger

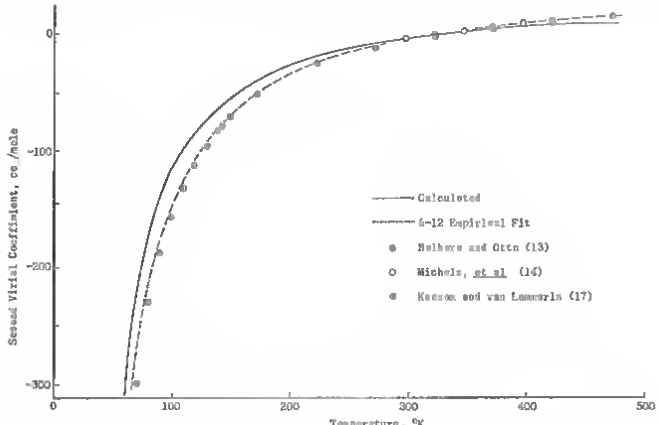


Figure 7. Second Virial Coefficient of N_2

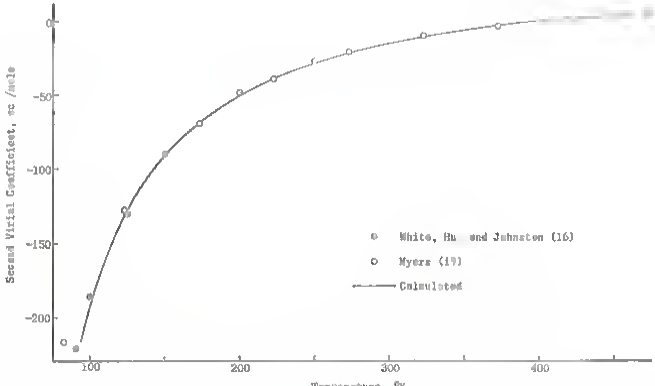


Figure 9 Second Virial Coefficient of O_2

in absolute value than the actual second virial coefficients at low temperatures because they did not use the third virial coefficient in their calculations From previous calculations, E^* was calculated to be 3 88 A and E^*/k was taken as 154 2°K These values were used to calculate the second virial coefficient from the 6-12 potential tables presented earlier and from the spherical shell potential tables of de Boer and Mazur for $r_0^* = 2\ 74$ These calculated curves are compared in Figure 9 with the experimental data and with curves calculated from Pitzer's correlation and the Berthelot equation which were discussed earlier It can be seen that the calculations for the spherical shell potential and the 6-12 potential are in excellent agreement with the experimental data and are considerably better than either of the curves from the Berthelot equation or Pitzer's correlation

Chlorine (Cl_2)

From previous calculations, E^*/k was found to be 438°K and E^* was 5 00 A for Cl_2 The value of r_0^* was found to be 2.52 Use of these parameters with the spherical shell potential tables of de Boer and Mazur led to the calculated curve in Figure 10 In the absence of reliable second virial coefficient data second virial coefficient curves from Pitzer's correlation and the Berthelot equation were calculated and are presented in Figure 10 for comparison The agreement at the Boyle point is quite good for all three curves This is remarkable when one considers the range in $(E^*/k)_{6-12}$ values that were used to calculate E^*/k for Cl_2 The agreement at low temperatures is not as good but is still acceptable If the Berthelot equation and Pitzer's correlation give the correct virial coefficients then it appears that the calculated E^* value for Cl_2 is slightly large

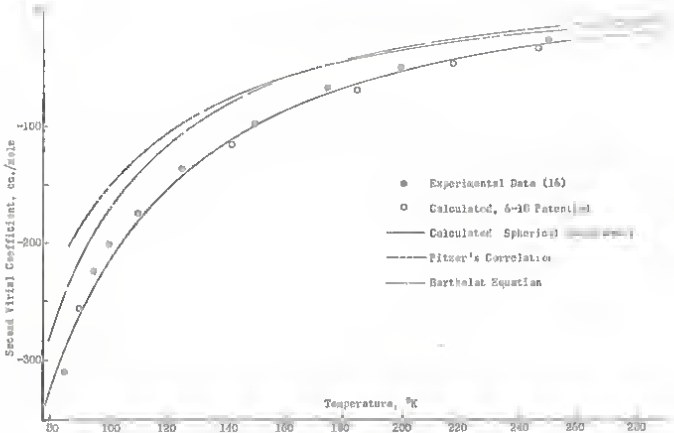


Figure 2. Second Virial Coefficient of F_2

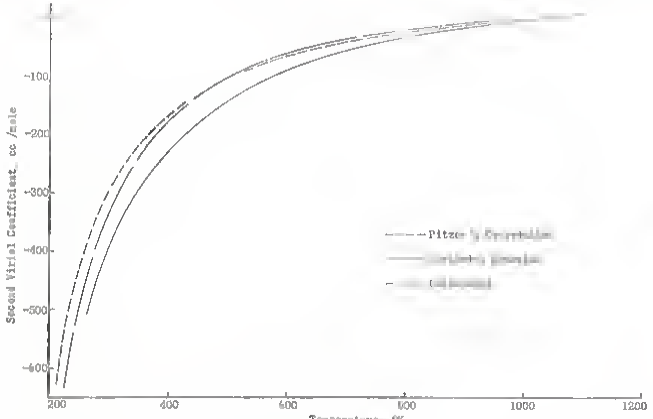


Figure 10 Second Virial Coefficient of Cl_2

From these calculations it appears that this method of calculating potential energy functions is valid, and that at least the size parameters used are satisfactory. Use of the energy parameters in calculations for more complex molecules should indicate whether they are satisfactory or not.

ane (C_2H_6)

In order to calculate potential energy functions of molecules containing methyl (CH_3) groups it is necessary to have parameters for this group. In view of the success of Cleary and Vanderslice (6) in treating methyl groups as single atoms this approach will be used.

Numans and Lambert (3) demonstrate that CH_4 can be correlated with the inert gases and diatomic molecules which seem close to fitting a 6-12 potential better than with more complex molecules such as CF_4. Pitzer (10) in his correlation found the acentric factor of methane to be 0.013, which indicates that the potential energy function should be close to a 6-12 potential. Therefore it seems reasonable to treat methane as an atom obeying the 6-12 potential in order to obtain parameters for a CH_3 group.

Cleary and Vanderslice, in their calculations, assumed that a CH_3 group interacts exactly like CH_4, and this is probably nearly correct. The approach taken here is to assume that $r^*_{CH_3} = r^*_{CH_4}$ and then to treat methane as though it were a diatomic gas composed of two methyl groups separated by the C - C bond distance in order to obtain the energy parameter for CH_3.

Parameters for CH_4 for the 6-12 potential are given in Table 13. The value of r^* taken for CH_3 is the mean of the values in that table.

$r^*_{CH_3} = 4.32$ A [illegible] as 0.770 A and the potential energy function was calculated from Equation 8. These calculations gave

$$R^* = 5.045 \text{ A}$$

$$\frac{\mathcal{E}^*_{C_2H_6}}{\mathcal{E}^*_{CH_3}} = 2.219$$

$$r^*_e = 3.28$$

The calculated potential energy function for C_2H_6 is presented in reduced form in Table 14 and in Figure 11. A 6-16 potential was found to fit the calculated curve very well and some points are plotted in Figure 11 for this potential. From Figure 3 it was determined that

$$\frac{\mathcal{E}^*_{6-16}}{\mathcal{E}^*_{6-12}} = \frac{3.41}{2.78} = 1.227$$

In order to evaluate $\mathcal{E}^*_{CH_3}$ it is necessary to have 6-12 potential parameters for C_2H_6. Hirschfelder Curtiss and Bird (1) list parameters from both gas viscosity and second virial coefficient data but Dix (20) states that the second virial coefficient data used was in error. Therefore only the parameters from gas viscosity measurements were used. These parameters for the 6-12 potential are

$$\mathcal{E}^*/k = 230^\circ\text{K}$$

$$R_e = 4.41\text{A} \text{ A}$$

$$R^* = 4.97 \text{ A}$$

Experimental second virial coefficient data for C_2H_6 is cited by Dix (20). The second virial coefficient was also calculated from Pitzer's correlation and from the Berthelot equation. These values of the second virial coefficient are given in Figure 12.

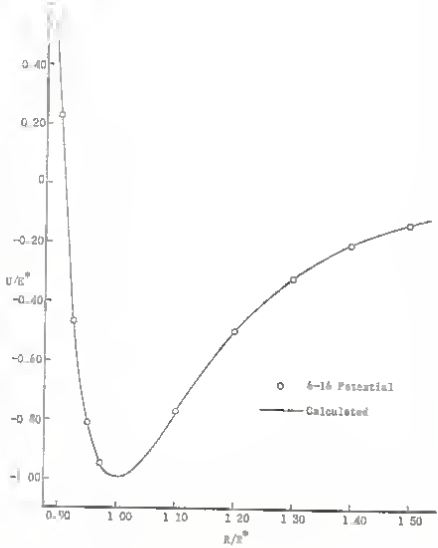


Figure 11 Potential Energy Function of C_2H_6

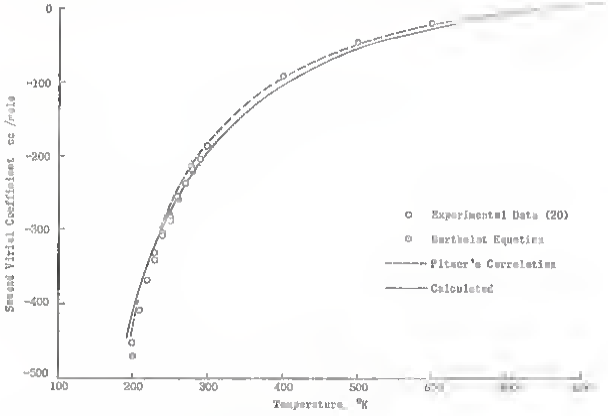


Figure 12 Second Virial Coefficient of C_2F_6

Empirically fitting 6-12 potential parameters to the experimental second virial coefficient data led to parameters which were unrealistic for the following reasons

1. The R^* value was empirically found to be approximately 7 A One would not expect this value to be larger than $R^*_{CH_4} + \rho = 5.86$ A

2. The calculated potential energy functions for all other molecules have given R^* values that were approximately correct. This value was 5.045 A

3. The value of R^* from gas viscosity was 4.97 A

4. The value of E^*/k obtained empirically was about 150°K as compared with 230°K from gas viscosity data. Methane has an E^*/k value of 144°K and it does not seem reasonable that the E^*/k value is about the same for C_2H_6

These data were also fitted with parameters for the spherical shell potential $r_0^* = 3.5$ and 3.0. These parameters were better but not completely satisfactory

The difficulty in fitting parameters to these data probably occurs because the data cover a temperature range of only 100°K and there are no values of the second virial coefficient near the Boyle point. Small errors in slope of the experimental curve have a large effect upon the size of the parameters under these conditions

Since Pitzer's correlation gives second virial coefficients that are close to the experimental values it probably is valid to use it to calculate the second virial coefficient over a wide range of temperatures. Using the value of the Boyle point and one other point from Pitzer's correlation with the calculated second virial coefficient for the 6-12 potential gave $E^*/k = 236$°K and $R^* = 5.10$ A. These parameters

[illegible] the most reasonable. For the 6-12 potential [illegible] the parameters are $\varepsilon^*/k = 215°K$ and $r^* = 5.45$ A.

Since this last method of calculation gave reasonable results, the following calculations were made using both Pitzer's correlation and the Berthelot equation to determine the Boyle temperature.

T_B, °K	Source
733	Pitzer's correlation
748	Berthelot equation
740	Average

$$(\varepsilon^*/k)_{6-12} = \frac{740}{3.41} = 217°K$$

Averaging this value of $(\varepsilon^*/k)_{6-12}$ with that from gas viscosity data gave the value

$$(\varepsilon^*/k)_{6-12} = 224°K$$

which was used to get the energy parameter for the methyl group

$$(\varepsilon^*/k)_{6-12} = 1.227\ (\varepsilon^*/k)_{6-12} = 275°K$$

Since it was previously found that

$$\frac{(\varepsilon^*/k)_{C_2H_6}}{(\varepsilon^*/k)_{CH_3}} = 2.219$$

the final result

$$(\varepsilon^*/k)_{CH_3} = \frac{275}{2.219} = 124°K$$

is obtained. Therefore the parameters used for CH_3 are

$$\varepsilon^*/k = 124°K$$

$$r^* = 4.32\ A$$

Use of the spherical shell model in these calculations rather than the 6-12 potential would have made only about 2 percent difference in the final value of ϵ^*/k. This certainly is well within the accuracy of the above calculations. The calculated value of ϵ^*/k for CH_3 is only 14 percent less than that for CH_4, in fair agreement with Clancy and Vanderslice's assumption that the two are the same.

The second virial coefficient calculated from these parameters and $r_0^* = 3.23$ for the spherical shell potential is shown in Figure 12 and is in reasonable agreement with those determined by other methods.

CHAPTER IV

CALCULATIONS FOR POLYATOMIC MOLECULES

In this section potential energy functions and second virial coefficients were calculated for polyatomic molecules using as parameters for the peripheral atoms the atomic parameters calculated from the diatomic gas data. The equations of Hanson and Lambert were again used to calculate the potential energy functions. For all interactions between dissimilar atoms, the following average parameters were used

$$\mathcal{E}^*_{AB} = \sqrt{\mathcal{E}^*_A \mathcal{E}^*_B}$$

$$r^*_{AB} = \frac{1}{2}(r^*_A + r^*_B)$$

where $\mathcal{E}^*_A$ and $\mathcal{E}^*_B$ are parameters for interactions between like molecules and $\mathcal{E}^*_{AB}$ is the parameter for interactions between molecules A and B. The subscripts have the same meanings with the r^* values.

The problem of choosing parameters for the central carbon atom in molecules like CF_4 and CCl_4, the central silicon atom in SiF_4 and $Si(CH_3)_4$, and the central sulfur atom in SF_6 is one that could only be solved by trial and error. Initial attempts to use the same parameters for carbon atoms as used for fluorine atoms caused calculated values of $\mathcal{E}^*/k$ for the molecules that were much too large, and it was concluded that parameters for carbon should probably be bounded by those for neon and helium. Likewise, the parameters for silicon and sulfur atoms should be bounded by those for argon and neon. Because of this

uncertainty in choosing parameters for these central atoms, three calculations were made for each molecule in this section. In order to avoid repetition of the parameters used in each calculation, the calculations were given a consistent set of code numbers that can be used to determine the parameters used quite easily. The parameters for the peripheral atoms were the same for all calculations for a given substance and are the ones determined from the diatomic gases. These parameters are

Peripheral atom	r^*_c, A	ε^*/k, °K
F	3.11	90.7
Cl	3.84	303
CH_3	4.32	124

For molecules involving carbon as the central atom, the following table gives the code numbers and parameters used

Code number	$(r^*)_C$	$(\varepsilon^*/k)_C$
1	$(r^*)_{Ne} = 3.11$ A	$(\varepsilon^*/k)_{Ne} = 35$ °K
2	$\frac{1}{2}\left[(r^*)_{Ne} + (r^*)_{He}\right] = 3.00$ A	$\frac{1}{4}\sqrt{(\varepsilon^*)_{Ne}(\varepsilon^*)_{He}} = 19.0$°K
3	$(r^*)_{He} = 2.85$ A	$(\varepsilon^*/k)_{He} = 10.2$°K

For example, calculation CF_4 - 1 used the fluorine parameters given above and neon parameters were used for the carbon atom.

For molecules involving silicon or sulfur as the central atom, the following table gives the code numbers and parameters used

Code number	$(r^*)_S$ or Si	$(\varepsilon^*/k)_S$ or Si
1	$(r^*)_{Ar} = 3.64$ A	$(\varepsilon^*/k)_{Ar} = 120°K$
2	$\frac{1}{2}\left[(r^*)_{Ar} + (r^*)_{Ne}\right] = 3.46$ A	$\frac{1}{k}\sqrt{(\varepsilon^*)_{Ar}(\varepsilon^*)_{Ne}} = 65.2°K$
3	$(r^*)_{Ne} = 3.11$ A	$(\varepsilon^*/k)_{Ne} = 38.0°K$

For example calculation $Si(CH_3)_4$ - 3 used the CH_3 parameters given above and each parameters for silicon

All potential energy functions were calculated using an electronic computer and the minimum in each of the potential energy curves was located by making calculations at intervals of 0.01 A near the minimum Table 16 contains a summary of the parameters determined in these calculations The calculations for each molecule are discussed separately below

CH_4

Several sets of calculations were made for methane but none resulted in calculated second virial coefficients that were even close to the experimental values Even when ε^*/k for carbon was taken as the same as that for fluorine atoms the calculated E^*/k was so small that the calculated second virial coefficients were only about one-half the size of the experimental values This result should not have been surprising because, as mentioned before, methane behaves more like a simple 6-12 potential atom than it does a quasispherical molecule with large interactions in the hydrogen atoms Since these calculations only demonstrated that methane can best be treated as a single center of interaction none of the calculations will be given here

The value of ρ for the fluorine atoms was the C - F bond length 1.323 A.

An interesting result of these calculations was that changing the parameters for carbon changed the values of E^*/k but had little effect on R^* or on the shape of the potential energy function when it is plotted on reduced coordinates. Figure 13 shows a potential energy function plotted from the calculations of CF_4 - 1 but the other two calculated potentials differed from it by a negligible amount. For this reason only one set of values of R/R^* and E/E^* will adequately represent all the calculated potential energy functions. The calculated values of E^*/k and R^* and the reduced potential energy function for these calculations are given in Table 17. Points plotted as Figure 13 for a 7-21 potential and for $r_0^* = 1.90$ for the spherical shell potential show that either could be used as an adequate empirical representation of the calculated potential energy function of CF_4.

In Figure 14, the three types of interactions that make up the potential energy of CF_4 are shown for CF_4 - 1. This figure shows that although the interactions between carbon and fluorine atoms are smaller than those between fluorine atoms, they are by no means negligible. The C - C interactions are quite small, however, and neglecting them would cause little error.

These calculations show why it is possible to make calculations based upon the potential energy function of molecules such as CF_4, but neglecting the carbon atom entirely. Neglecting the carbon atom will not change the shape of the potential energy function appreciably and as long as the parameters E^*/k and R^* are evaluated empirically, an

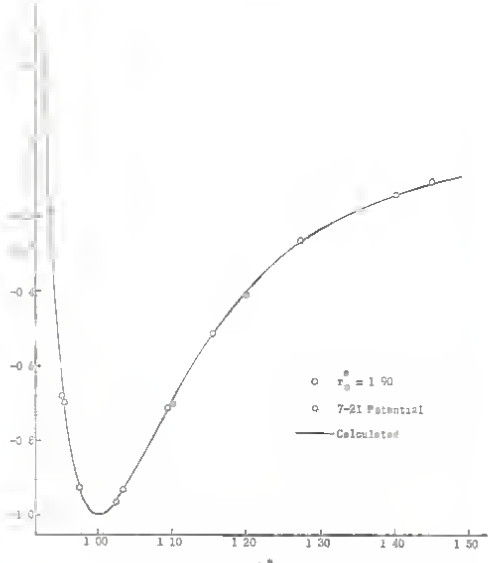


Figure 13 Potential Energy Function of CF_4

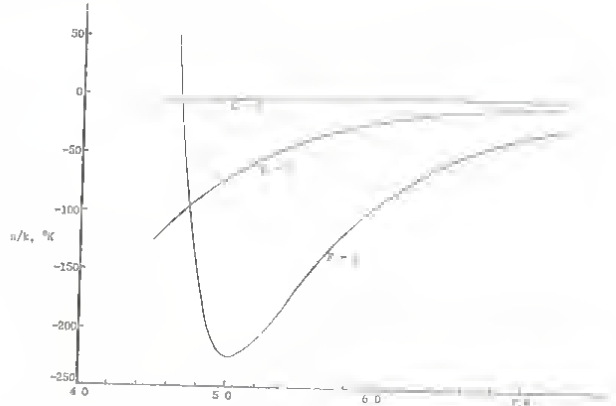


Figure 14 Components of Potential Energy

accurate potential energy function can be obtained. In fact, when one neglects the carbon atom entirely, the spherical shell model parameter is 1.90 (an exact fit), which also fits (empirically) the potential energy function when carbon interactions are included. This explains the success of Hoover and de Reese's (8) correlation of second virial coefficients using the spherical shell model and of Clancy and Vanderslice's (4) calculations of potential energy functions without considering carbon interactions.

In Figure 13 experimental values of the second virial coefficient by Hamann and Lambert (3) are shown, along with calculated second virial coefficients from Pitzer's correlation and the Berthelot equation. Also shown are the calculated curves using parameters from calculations $CF_4 - 1$ and $CF_4 - 2$ and the value $r_0^* = 1.90$ for the spherical shell model. As can be seen, the calculation for $CF_4 - 2$ fits the data better than for $CF_4 - 1$, although both are of the right order of magnitude. It appears that the calculated value of R^* is slightly larger than the best fit to the experimental data and that the actual E^*/k should be somewhere between those from $CF_4 - 1$ and $CF_4 - 2$ calculations. This is borne out by the fact that a good fit (by eye) to the experimental data can be obtained using $R^* = 4.70$, $E^*/k = 281°K.$, and $r_0^* = 1.90$ for the spherical shell potential.

Pitzer's correlation comes very close to the experimental data over the entire range of temperature, but the Berthelot equation is in considerable error at high temperatures. The second virial coefficient from calculation $CF_4 - 3$ was not as good as for $CF_4 - 1$ and $CF_4 - 2$ and is not shown or discussed further.

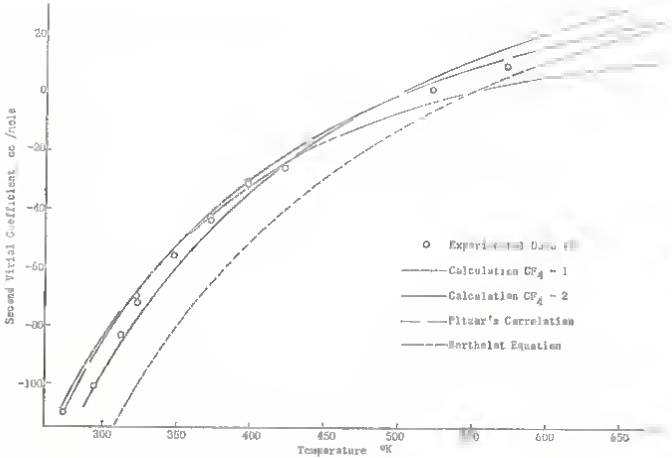


Figure 15 Second Virial Coefficient of CF_4

C_2F_6

The value of ρ used for the fluorine atoms was the distance from the center of the C - C bond to the fluorine atoms, which was calculated from bond lengths and angles for the C_2F_6 molecule. The value of ρ for the carbon atoms was half the C - C bond length. The values used were

$$\rho_F = 1.749 \text{ Å}$$

$$\rho_C = 0.770 \text{ Å}$$

Again, the shape of the potential energy functions from the different calculations differed by a negligible amount. The R^* and E^*/k values for each calculation and the common reduced potential energy function are given in Table 18. The calculated potential energy function is given in reduced form in Figure 16 and can probably be adequately represented by using $r_0^* = 1.6$ for the spherical shell potential.

Experimental second virial coefficients for C_2F_6 are cited by Reed (21) and are shown in Figure 17. Also given in this figure are curves calculated from Pitzer's correlation and from the Berthelot equation. Curves calculated from the parameters of C_2F_6 - 1 and 2 using $r_0^* = 1.60$ for the spherical shell potential are also shown. The calculated curve for C_2F_6 - 1 agrees very well with the Berthelot equation and Pitzer's correlation and approaches the experimental data at lower temperatures. The calculated curve for C_2F_6 - 2 is in better agreement with the experimental data at high temperatures, but deviates at lower temperatures. None of the calculated second virial coefficient curves predicts such a rapid change in second virial coefficients as is shown by the experimental data. Although adjustment of the parameters for carbon atoms could make the calculated curves pass through the experimental data, it does not appear likely that any calculated curve would fit these data over the entire temperature range.

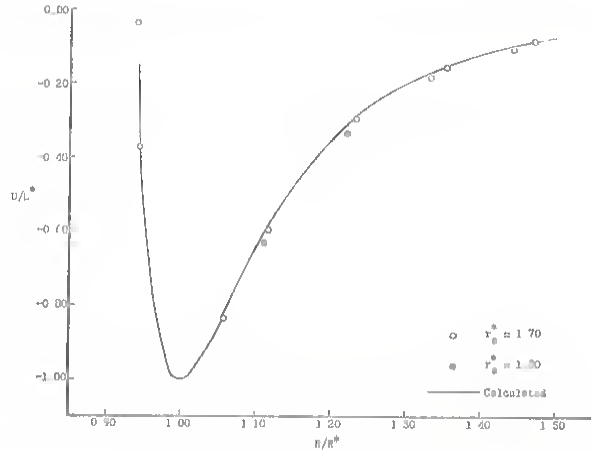


Figure 16 Potential Energy Function of C_2F_6

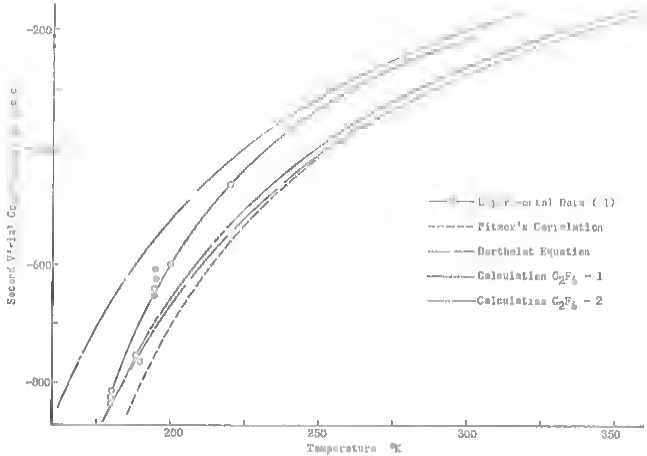


Figure 17 Second Virial Coefficient of C_2F_6

Parameters for C_2F_6 for the 7-28 potential evaluated from gas viscosity measurements by McCubbrey and Singh (22) are

$$R^* = 5.35 \text{ Å}$$
$$E^*/k = 384°K$$

This value of E^*/k agrees fairly well with the value 352.2°K from C_2F_6 - 2 but the value of R^* is considerably smaller than the values 5.81 Å from C_2F_6 - 1 and 5.825 Å from C_2F_6 - 2. As might be expected because of this low value of R^* these parameters from gas viscosity do not fit the second virial coefficient as well as calculations C_2F_6 - 1 and 2

CCl_4

The value of ρ used for the chlorine atoms was the C - Cl bond length 1.766 Å. Again, changing carbon parameters did not change the shape of the potential energy function. The calculated values of R^* and E^*/k for the three calculations and the common reduced potential energy function are given in Table 19. The potential energy function from these calculations is given in Figure 18 where points plotted for $r_e^* = 1.8$ for the spherical shell potential show that $r_e^* = 1.8$ gives a satisfactory fit to the calculated curve.

Experimental second virial coefficients of CCl_4 have been reviewed by Prengle and McGlashan (23), and the curve representing the experimental data is their most probable curve through all the data. In Figure 19 the experimental second virial coefficient curve is shown along with curves calculated from Pitzer's correlation and the Berthelot equation. Also shown are curves calculated from the parameters of calculations CCl_4 - 1 and 2 using $r_e^* = 1.8$ for the spherical shell model

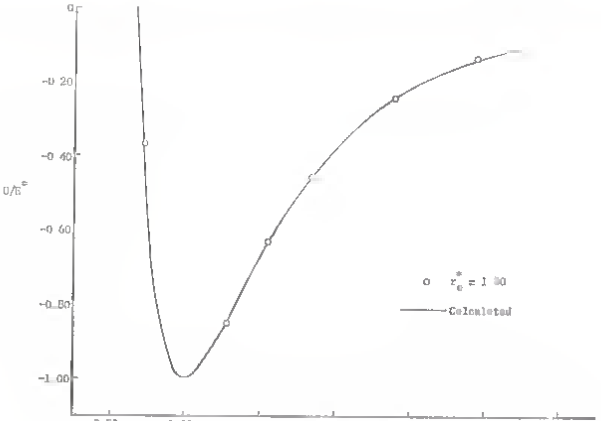


Figure 10 Potential Energy Function of CCl_4

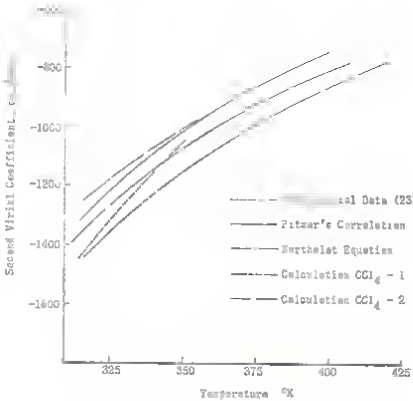


Figure 19. Second Virial Coefficient of CCl_4

...es of the calculated curves match the slope of the experimental data but all are close in magnitude The calculated curve for CCl_4 - 2 fits the experimental data at higher temperatures but deviates at lower temperatures and is better than Pitzer's correlation or the Berthelot equation over the range of the data The curve calculated for CCl_4 - 1 approaches the experimental data at the lower temperatures The experimental second virial coefficients are available over such a narrow range of temperature that one should not place too much importance on the difference in slope between calculated and experimental curves

$C(CH_3)_4$

The value of ϵ for the CH_3 groups was the C - C bond length 1 5dl A The calculated R^* and E^*/k for the three calculations are given in Table 20 along with the common reduced potential energy function The calculated potential energy function is shown in Figure 20 where it is shown that the spherical shell potential for $r_s^* = 2$ 10 fits the calculated curve very well

Experimental data on the second virial coefficient of $C(CH_3)_4$ is given by Hamann and Lambert (3) These data are shown in Figure 21 along with curves calculated from Pitzer's correlation and the parameters from calculation $C(CH_3)_4$ - 1 and the spherical shell potential for $r_s^* = 2$ 10 The Berthelot equation gave a curve essentially the same as Pitzer's correlation and is not shown The agreement among all curves shown in Figure 21 is excellent especially when considering that a temperature range of 300°K is covered

$C_2(CH_3)_6$

The value of ϵ used for the CH_3 groups was calculated from hand

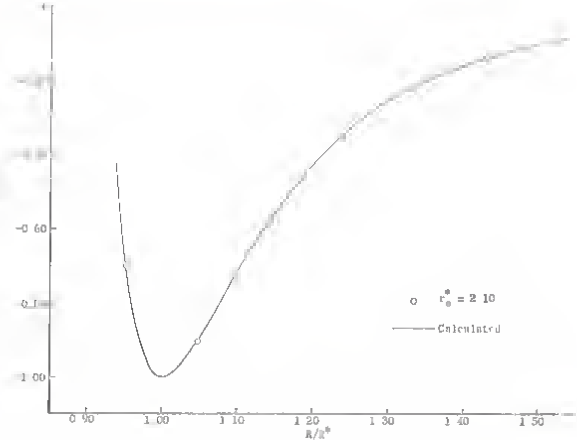


Figure 20 Potential Energy Function of $C(CH_3)_4$

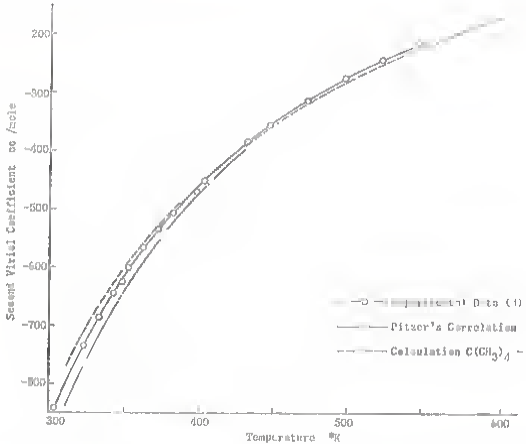


Figure 21 Second Virial Coefficient of $C(CH_3)_4$

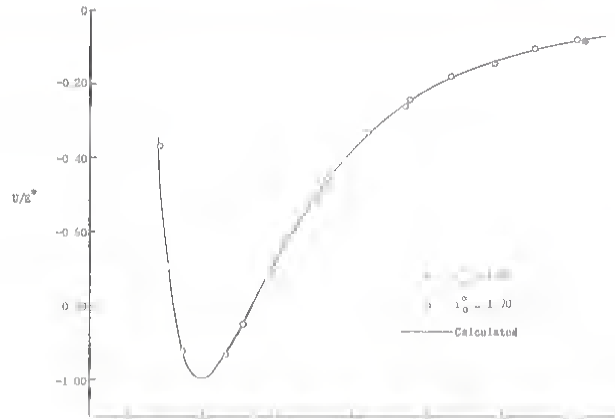
lengths and angles and was 1 939 A The value of ρ used for the inner carbon atoms was 0 770 A The calculated E^* and E^*/k values for the three calculations and the common reduced potential energy function are given in Table 21 The potential energy function is plotted in Figure 22 along with points for the spherical shell potential for $r_0^* = 1\ 8$ and 1 9 The calculated curve lies between $r_0^* = 1.8$ and 1 9 and a good fit would probably be $r_0^* = 1\ 85$

In the absence of experimental second virial coefficient data, curves calculated from Pitzer's correlation and the Berthelot equation are compared with the curve for calculation $C_2(CH_3)_6 - 1$ and 2 parameters and $r_0^* = 1\ 85$ for the spherical shell potential as shown in Figure 23 All of these curves are in reasonable agreement

SF_6

The value of ρ used for the fluorine atoms was the S - F bond length 1 584 A Since only calculation $SF_6 - 3$ gave reasonable results the potential energy function in Figure 24 and Table 22 applies only to this calculation Also shown in Figure 24 are points for the spherical shell potential for $r_0^* = 1\ 7$ and 1 8 and it can be seen that $r_0^* \simeq 1\ 75$ for the spherical shell potential should fit the calculated curve satisfactorily

Experimental second virial coefficients from several sources are cited by Reed (21) and these points are plotted in Figure 25 The correlation of Pitzer and the Berthelot equation gave practically identical results, so only the results of the calculation from Pitzer's formulation are shown in this figure Also given in Figure 25 is the curve for calculation $SF_6 - 3$ using $r_0^* = 1\ 75$ for the spherical shell


0
-0.20
-0.40
-0.60
-1.00
U/E*
Calculated

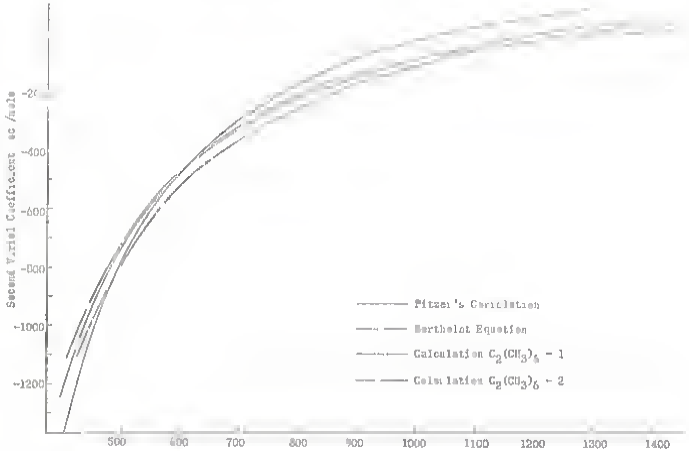
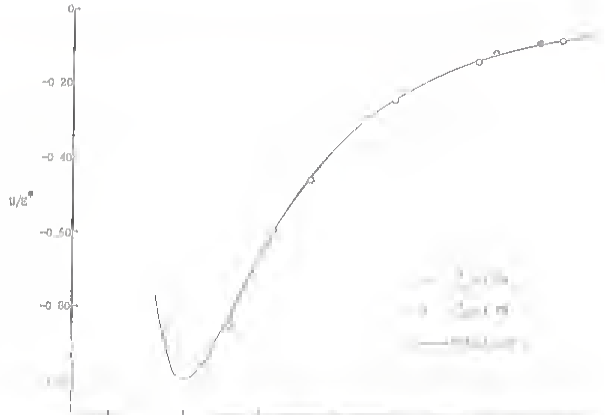


Figure 23 Second Virial Coefficient of $C_2(CH_3)_6$


0
-0 20
-0 40
-0 60
-0 80
u/e*
1 00
1 30
90°

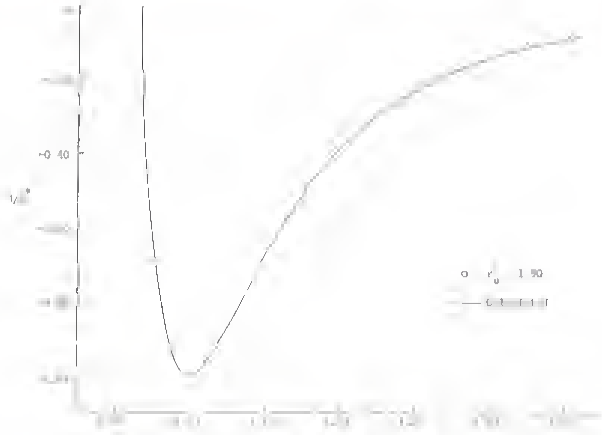
[illegible] Pitzer's Correlation comes very close to the experimental data and the calculated curve for SF_6 - 3 differs from the experimental data by only about 10 percent

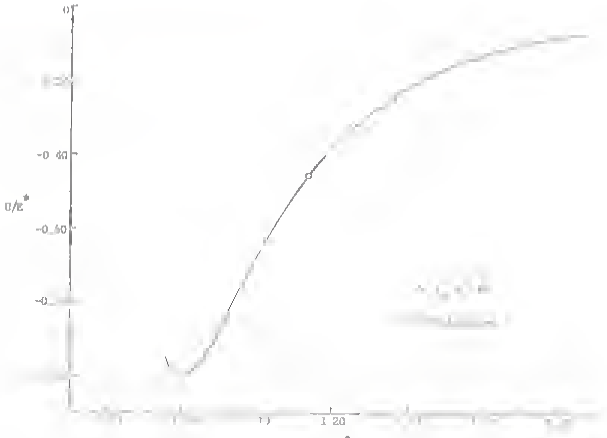
Since the parameters used for sulfur in the calculations that gave the only reasonable results were those for neon, not those for argon, this should be discussed further In all of the molecules discussed up to SF_6, the central atom or atoms contained eight shared electrons in the outer shell For SF_6 however, there are twelve electrons in the outer shell This expanded outer shell leads one to suspect that the electrons are bound more closely to the fluorine atoms rather than to the sulfur atom If one thinks of these six electrons in the outer shell as "belonging" to the fluorine atoms, then one has left in the center of the molecule what is essentially a neon atom since interactions between atoms are due mainly to electrons This explanation is rather solves as are all of these calculations, but nevertheless it does fit the result of the calculations

SiF_4

The value of ρ used in these calculations was the Si - F bond length 1 561 A

Since the energy parameter for silicon is quite large, changing this parameter had some effect on the shape of the reduced potential energy curves The two calculations which gave reasonable results were SiF_4 - 1 and 2, and the E^*/k and R^* values are given along with the reduced potential energy functions in Table 23 The reduced potential energy curves are shown in Figures 26 and 27 The potential energy function from SiF_4 - 1 can be fitted reasonably well by the spherical 11 potential for r_0^* = 1.9 as shown in Figure 26. The potential


-0.40
1.90


0
-0.40
U/E*
-0.60
-0
1.20
R/R*

energy function for SiF_4 - 2 fits the spherical shell potential for $r_0^* = 1$ Å as shown in Figure 27

Experimental measurements of the second virial coefficient of SiF_4 have been made by Ramaux, McKenaney and Pearce (24) and are shown in Figure 28 along with calculated curves from Pitzer's correlation and the Berthelot equation. Also shown are the calculated curves for SiF_4 - 1 and 2 using the values of r_0^* for the spherical shell potential that are given above. Pitzer's correlation fits the data very well and the Berthelot equation less well. The calculated curves from SiF_4 - 1 and 2 were not very close to the experimental data, but one gives high values and one gives low values of the second virial coefficient. These two curves appear to have the same shape as for Pitzer's correlation and the experimental data, which indicates that the shape of the potential energy function and the values of R^* are probably nearly correct. There is a very large difference in the E^*/k values from the two calculations which is the reason for the large difference between the curves for SiF_4 - 1 and 2. A value of E^*/k of about 300°K would be more reasonable than either of the values 348.2°K and 252.1°K that were calculated. This indicates that the proper parameters for silicon in SiF_4 should be slightly smaller than those for argon, but not as small as those used for SiF_4 - 2.

$Si(CH_3)_4$

The value of σ used in these calculations was the Si - C bond length, 1.909 Å. The calculated potential energy function for $Si(CH_3)_4$ - 1 is given in Table 24 and in Figure 29. The spherical shell potential for $r_0^* = 1.90$ is shown in Figure 29 to fit the calculated potential very well.

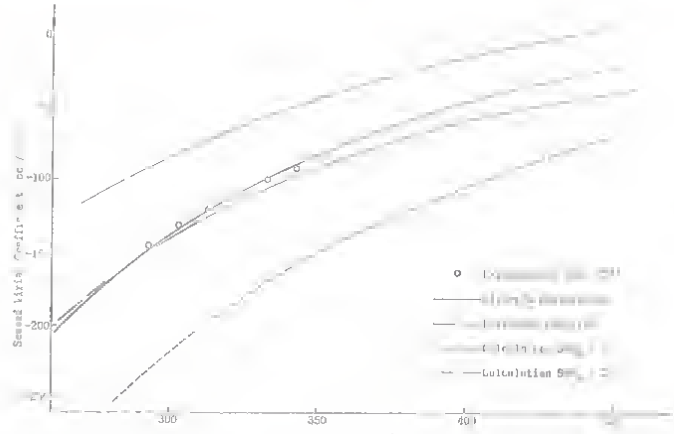
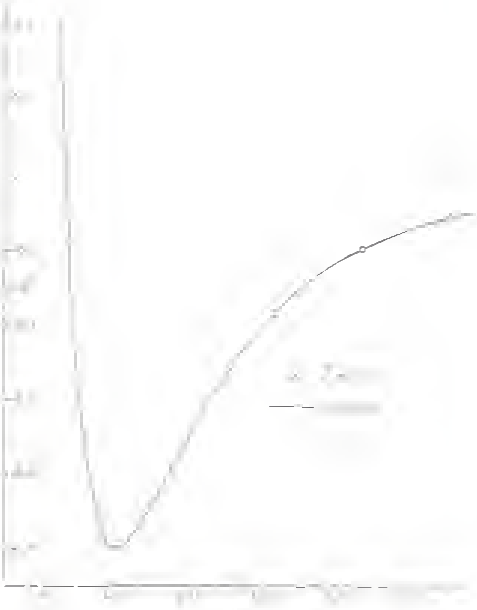


Figure 28 Second Virial Coefficient of SiF_4



[illegible] of $Si(CH_3)_4$ has been measured by [illegible] Lambert and Thomas (25) and is shown in Figure 30 The results of calculations o[illegible] second virial coefficients from Pitzer's correlation and the Berthelot equation were very close together so only the results of the calculation from Pitzer's correlation are shown in Figure 30 Also shown in this figure is the curve calculated from the parameters of calculation $Si(CH_3)_4$ - 1 using $r_e^* = 1$ 90 for the spherical shell model This latter curve is in unusually poor agreement with the experimental data, the calculated values being about 60 percent of the size of the experimental values of the second virial coefficient In view of the past success of this type of calculation It would appear that a numerical error in the calculation had been made but a careful check of this calculation and comparison with other calculations showed that no error had been made Since the calculated and experimental curves become farther apart at lower temperatures it appears that both the calculated R^* and E^*/k values are too small for this molecule Comparison with an empirical fit of the spherical shell model to these same data by de Rocco and Hoover indicates that the calculated E^*/k should have been about 450°K instead of 388 3°K and R^* should have been about 7 5 Å instead of 7 04 Å Evidently some of the parameters used in this calculation are not even approximately correct for this molecule but there is no obvious reason why this should be so One would think that the same silicon parameters that were used for SiF_4 would be correct and that the CH_3 parameters used for $C(CH_3)_4$ would also be the same for $Si(CH_3)_4$ The value of ε used was the average of two experimental determinations and should be approximately correct There is of course the possibility that this method of calculation is not realistic for this molecule

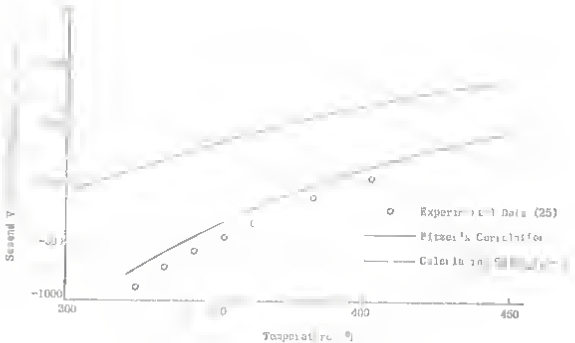


Figure 30 Second Virial Coefficient of $Si(CH_3)_4$

just as it [illegible] In fact the results of the calculations for CH_4 and $Si(CH_3)_4$ [illegible] second virial coefficients that were much too small [illegible] at is obvious that these calculations for $Si(CH_3)_4$ do approximate the potential energy function for this molecule

SUMMARY AND DISCUSSION

The purpose of the calculations in Part I has been to calculate potential energy functions for several polyatomic molecules and then to test these potential energy functions by calculating second virial coefficients and comparing with experimental data. Since it is easy to lose sight of the purposes of each step in the calculations and how it fits into the total, the following step-wise summary is given.

1. Using the equations of Hamann and Lambert (3) and r^* values from inert gases, reduced potential energy functions for the diatomic gases H_2, N_2, O_2, F_2, Cl_2, and C_2H_6 were calculated.

2. Using these calculated potential energy functions and 6-12 potential parameters from experimental data on these diatomic gases, energy parameters for hydrogen, fluorine, chlorine atoms and methyl groups were determined. The size parameters chosen for the atoms in these calculations were tested by calculating second virial coefficients and comparing with experimental data.

3. Using the equations of Hamann and Lambert and the atomic parameters determined from the diatomic gases, potential energy functions were calculated for CF_4, C_2F_6, CCl_4, $C(CH_3)_4$, $C_2(CH_3)_6$, SF_6, SiF_4, and $Si(CH_3)_4$.

4. These latter potential energy functions were tested by calculating second virial coefficients and comparing with experimental data.

These calculations were made by empirically fitting spherical shell potentials to the calculated potential energy functions and then using the tables of de Boer and Mazur (8) to calculate second virial coefficients.

Results of these calculations will now be discussed in more detail.

Calculations for the diatomic gases showed that their potential energy functions are indeed not very much different in shape from the 6-12 potential but this difference increases with the size of the molecule. For example the potential energy function of hydrogen could be adequately represented by a 6-14 potential while that of chlorine required a 6-20 potential. The calculated R^0 values for the diatomic gases were in good agreement with R^0 values that would be determined from second virial coefficient data which indicates that the size of the atoms in these molecules is not much different from the size of the corresponding inert gas. The energy parameters for the fluorine and chlorine atoms determined from the diatomic gas data gave good results when used in more complex molecules which indicates that the treatment of diatomic gases as dumbell-shaped, freely-rotating molecules is adequate.

Calculations for methane which involved the assumption that there were interactions in the constituent hydrogen and carbon atoms were unsuccessful in giving reasonable parameters for the potential energy function. This result confirmed the findings of other authors that methane can best be treated as a single atom which interacts according to a 6-12 potential. The calculations for ethane and other molecules containing methyl groups showed that treating methyl groups as though they were single 6-12 centers of interaction was an adequate method of approach. which again confirms the findings for methane.

The calculations for other polyatomic molecules containing carbon as the central atom (but no hydrogen atoms) showed that only the C – C interactions could safely be ignored. Changing parameters of the carbon atom had very little effect upon the shape of the resulting potential energy function or the value of β^* but did have a larger effect upon the value of E^*/k. This result of the calculations indicates that consideration of only the peripheral atoms as in the spherical shell model will give a potential energy function that has approximately the correct shape. If the E^*/k and R^* parameters are then determined empirically, a reasonable potential energy function should be obtained.

In these calculations it was found that reasonable results could be obtained using mean parameters for carbon, although in some cases better results were obtained using parameters midway between those of neon and helium. In no cases were helium parameters found to be better than those for carbon. The parameters determined from the diatomic gases were used for the peripheral atoms, and in view of the success of these calculations, they must have been approximately correct.

There was more difficulty in getting good results for the molecules containing silicon and sulfur as the central atoms because the interactions involving the central atoms form a large part of the total interaction, and the choice of reasonable parameters was more important than it was for carbon as the central atom. For SiF_4 reasonable results could only be obtained by using parameters that were smaller than those for argon (probably about 20 percent smaller), while for SF_6 it was necessary to use neon parameters for sulfur. This latter assumption was justified by assuming that because of the twelve electrons in the outer shell these electrons would be considered as "belonging" to the fluorine

[illegible]ssuming essentially a neon atom at the center. Calculations for $Si(CH_3)_4$ were not successful at all. Both K° and E°/k parameters obtained were too small.

In most cases the calculated second virial coefficients did not exactly match the experimental data, but for almost all of these cases no better agreement could have been obtained by arbitrarily adjusting the parameters estimated for the central atoms. It was felt that the calculations showed that reasonable approximations to the potential energy functions were obtained by using a set calculation procedure, and further arbitrary adjustments would serve no useful purpose in this respect.

As an interesting sidelight of these calculations, it was shown that Fitzer's correlation yielded very good estimates of the second virial coefficients of these molecules. The Berthelot equation was found to give good estimates of the second virial coefficient at low temperatures, but was not as good at temperatures around the Boyle point.

Since these calculations gave reasonable results in all but one case, it can be assumed that the interactions between many simple polyatomic molecules in the gas phase can be explained by assuming that they contain multiple centers of interaction, and that this assumption can be used in a quantitative as well as a qualitative manner.

PART II

POTENTIAL ENERGY FUNCTIONS AND THE LIQUID STATE

MEASUREMENT OF $(\partial P/\partial T)_v$ AT LOW TEMPERATURES

The thermal pressure coefficient $(\partial P/\partial T)_v$ has been measured [illegible] 31 32) for several organic liquids at temperatures above °C The The apparatus used for these measurements is essentially a constant-volume thermometer enclosed in a pressure bomb. The liquid sample is placed in a sample cell and sealed in with mercury. The temperature is held constant and the pressure outside the mercury seal is adjusted to give a certain volume of liquid inside the cell This procedure is repeated at several temperatures without removing the sample so that a series of temperature and pressure readings at essentially constant volume is obtained In general, it was found that the pressure varies linearly with temperature to give an observed value of $(\Delta P/\Delta T)$ This observed value is then corrected for small changes in cell volume arising from the temperature and pressure changes

The measurements cited above were made either above or just below room temperature so that the temperature could be controlled easily by conventional means In the present work, the thermal pressure coefficient for CF_4 and CH_4 were measured. The triple point of CF_4 is at 89.5°K, and its normal boiling point is at 145.2°K, both of which are below the freezing point of mercury and well below room temperature Because of the low temperatures at which the apparatus was to operate in the present work it was necessary to change the design of the apparatus

[illegible] those used by previous experimenters. [illegible] a constant-volume cell was retained.

A schematic diagram of the apparatus used in the present work is given in Figure 3. The sample cell was an 0.5-inch o.d. by 0.402-inch i.d. nickel tube filled with 3/16-inch o.d. helices of 24 SWG nickel wire and had a capacity of about 6 cc. Two nickel pellets were added to help reduce temperature gradients across the cross-section of the tube. The top of the sample tube was silver-soldered to a nickel connecting piece into which a brass bellows-seal valve was screwed. The valve was not available in an angle pattern, and it was necessary to have a gear mechanism to permit turning the valve remotely from above. The valve was helium leak-tested both at the seat and bellows at the factory before shipment, and the valve was installed so that the stem side faced the sample cell. The bottom of the sample cell was closed by a flexible aluminum bellows. There were brass inner and outer aluminum bellows stops to prevent damage to the bellows by over extension or compression. A contact was so placed that the bellows made contact at zero pressure differential. The contact was connected to an indicator described by Mills (23), which was more sensitive than the conventional electric lamp indicator. A heavy-wall copper cylinder enclosed the sample cell to form a pressure cell. Helium was used to provide pressure, and entered the cell through a 3/16-inch o.d. steel brass steel tube. Temperature was measured on the outside of the sample cell by a thermocouple which entered the pressure cell through the pressure tubing. The wires to the contact also entered through this tube. Connection to the sample cell from a glass vacuum system was also made through 3/16-inch o.d. stainless steel tubing. The apparatus was enclosed by a heavy bronze can

[illegible] $(\partial^2 P/\partial T)_V$

1 Make to [illegible] brass bellows [illegible] valve (screwed into part 3)

2 Valve turning mechanism

3 Nickel connection for pressure cell and sample cell

4 Heavy-walled copper pressure cell (threaded to fit part 3)

5 Nickel sample cell, 1/2-inch o.d. x 4.2 inches long, filled with nickel helices Silver soldered to part 3

6 Nickel helices

7 Compass to indicate pressure balance

8 3/16-inch o.d. stainless steel tubing connection to pressure cell Molium adapted to pressure cell through this tube Thermocouple M-1 and wires for contact water through this tube

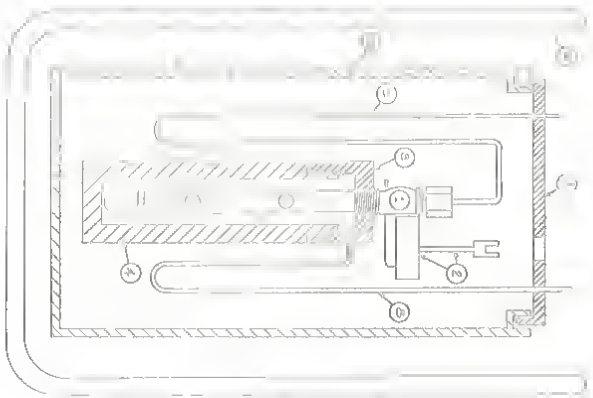
9 3/16-inch o.d. stainless steel tubing connection to sample cell

10 Heavy bronze can

11 Cap to bronze can

12 Dewar flask

Denotes position of thermocouples



and the entire [illegible] The lid to the [illegible] meltleg solde[illegible]

Operation [illegible]

1 The [illegible] ary helium

2 The [illegible] was evacuated

3 Liquid nitrogen was poured into the dewar flask so that it contacted the metal can, cooling the apparatus The approximate temperature of the can was measured by a thermocouple on the side of the can

4 When the entire apparatus was at approximately the desired temperature and cooling had slowed to a very slow rate, a sample of liquid was distilled into the sample cell from a glass vacuum system to which the cell was connected

5 After all liquid nitrogen had evaporated and the temperature began to drift slowly upward the valve was shut by use of a removable rod inserted into the valve-turning mechanism

6 From 50 to 100 psi of helium was admitted to the pressure cell from a cylinder of high-pressure helium through a system of needle valves which could be used either to introduce helium into or exhaust helium from the pressure cell The introduction of helium compressed the bellows and opened the contact circuit

7 The temperature was allowed to drift slowly upward, and when the indicator signaled that the bellows was at the contact point the e m f of the thermocouple inside the pressure cell and the pressure were recorded

8 Fifty to 100 psi more pressure was put on the cell, and the e m f and pressure when the bellows again made contact were recorded

[illegible] requested us if the [illegible] was ob[illegible] psi [illegible] [illegible] red to withstand 1,500 psi in the [illegible] cell [illegible] [illegible] and nitrogen was added to the dewar [illegible] [illegible] again. Helium was released from [illegible] [illegible] that the helium [illegible] app[illegible]

O[illegible] apparatus reached the temperature at which the valve had been originally shut, the valve was opened and the sample was either distilled out of the apparatus or left in for another measurement.

Pressure measurements were made on a Martin-Decker precision test gage which was factory calibrated to read accurately to ±0.15 percent of full scale (1,500 psi), i.e., ±2.25 psi gage pressure. The gage pressure scale could be read to within 1 psi, and pressure differences could probably be measured more accurately than the ±2.25 psi guaranteed.

Thermocouple emf values were measured on a Leeds and Northrup type K2 potentiometer upon which emf measurements of ±0.0001 mv can be made. Measurements of ±0.0001 mv can be made on a single day but the variation from day to day is more than this amount.

Temperature measurements were made using calibrated copper-constantan thermocouples. Thermocouple M-1 was in the pressure cell on the wall of the sample cell and thermocouple M-8 was on the side of the brass valve. These two thermocouples were found to give the same emf at the normal boiling point of liquid nitrogen and at the sublimation point of carbon dioxide at 1 atm pressure. Therefore, a single calibration equation applies to both thermocouples.

[illegible] orted against the vapor pressure of [illegible] pressure apparatus of Crowder (34) [illegible] calibration were analyzed chromat- [illegible] to contain only trace impurities as [illegible] a negligible error The following [illegible] was fitted by least squares to thirty-seven vapor pressure points for thermocouple M-8

$$t = -43.657 + 0.28189e - 4.9134e^{2} \qquad -182°C \leq t \leq -100°C \quad (33)$$

where t = Temperature, °C

e = e.m.f. mv.

This equation also applies to thermocouple M-1 and should yield the absolute temperature to ±0.05°C The temperature coefficient of the thermocouples was determined by differentiation of the above equation to be

$$\frac{dt}{de} = 0.28189 - 9.8272e \qquad °C/mv \quad (34)$$

The contact indicator used a tungsten over mercury tube and because the contact was confined to the area of the tube the current through the contact was very small Much of the pitted sparking sticking and surface fouling Mills (33) claims that any type of indicator will give a reproducible point at first contact to within 4 millionths of an inch

The bellows purchased from the Servometer Corporation had a spring constant of 9.5 pounds per square inch per inch change in length and an average internal cross-sectional area of 0.0314 square inches From the coefficient of thermal expansion of CF_4 the size of the cell and the cross-sectional area of the bellows it was determined that the

extra st[illegible] [illegible]ers should be about 0 03 inches per °K This means that the error in temperature read at the time of contact because of non-reproducible cus ect indication should be about 1 4 x 10^{-4}°K which [illegible] certainly negligible The spring constant of the bellows was low [illegible] pressure errors because of tension is the bellows could also be neglected

Corrections for the change in volume of the cell because of temperature ars pressure changes can be made in the following manner (31) The change in internal volume of the cell is

$$\Delta V = V\alpha_s \Delta T - V\beta_c \Delta P \qquad (35)$$

where ΔV = Change is volume of cell

V = Volume of cell

α_s = Coefficient of thermal e pansion of metal in cell

β_s = Compressibility of metal in cell

If $\Delta V = 0$ then $\Delta P/\Delta T$ observed is not correct and equal to $(\partial P/\partial T)_V$ Since this is not the extra pressure $\Delta P - \Delta P_{obs}$ would have to be applied to the liquid to compensate for ΔV That is

$$\Delta P - \Delta P_{obs} = \frac{\Delta V}{V\beta} \qquad (36)$$

where ΔP_{obs} = Observed value of ΔP

β = Compressibility of liquid in cell

When Equations 35 and 36 are combined

$$\left(\frac{\Delta P}{\Delta T}\right)_V = \left(\frac{\Delta P}{\Delta T}\right)_{obs} \left(1 - \frac{\beta_s}{\beta}\right) + \frac{\alpha_s}{\beta} \qquad (37)$$

Consideration was given to the amount of liquid inside the brass valve seat which is pumped in the usual amount of liquid in the small tube leading to the cell to compensate the difference in thermal expansion of the

[illegible]

[illegible] pres[illegible] β_c and β_c [illegible] to the values for [illegible]

For [illegible]

$$\frac{\beta_c}{\beta} \cong 5 \times 10^{[illegible]}$$

since β_c will [illegible] temperatures [illegible] mental values [illegible] available [illegible] temperatures this correction will be smaller but uncertain at lo[illegible]res. Because failure to make this correction would cause a[illegible] error of about 0.5 percent in the final result and other erro[illegible] more significant this correction was not made for any [illegible] in the present work.

The thermal expansion [illegible] as much as a 3 percent correction and [illegible] expansion at low temperatures [illegible] was done for all measurements. An equation [illegible] of nickel from which the following equation [illegible] of thermal expansion for nickel was derived [illegible] Critical Tables (36)

$$\alpha = \frac{3(\alpha + 2\beta t + [illegible])}{1 + \alpha t + \beta t^2 + \gamma t^3 + \delta t^4} \qquad -200^{\circ}C < t < 0^{\circ}C \qquad (35)$$

where the constants for nickel are

$\alpha = 12.5 \times 10^{-6}$ [illegible]

$\beta = 8.75 \times 10^{-9}$ [illegible]

[illegible]

[illegible] ochical coefficients of thermal [illegible]

[illegible] measurements of the pressure, work [illegible] uniformity of temperature in [illegible] temperature rise this will [illegible] measurements made. Experimental measurements [illegible] CF_4, and CH_4, and the measurements for each of th[illegible] be discussed separately.

CCl_4

Technical grad[illegible] a batch laboratory fractionating column [illegible] when distilling [illegible] [illegible] be used in these experiments. [illegible] material was measured with a calibrated [illegible] published vapor pressure [illegible] the sample was pure enough for use.

The measu[illegible]. The rate of temperature rise [illegible] 0.013°C/min in the other [illegible] apparatus should have been [illegible] measurements. The temperatu[illegible] from that measured [illegible] constant during [illegible] not change rapidly [illegible] remain [illegible] measurements.

[illegible] ... ures the [illegible] ... mode [illegible] the rate ... [illegible] from about 0.043°K/[illegible] to about 0.027°K/min at 97°K. [illegible] were probably [illegible] large temperature gradients across the [illegible] the sample cell. The actual [illegible] drift [illegible] apparent rates [illegible] to the cell caused [illegible]. This [illegible] apparent because [illegible] surface of the cell [illegible]. The cell temperature then remained constant [illegible] to drift up [illegible] again. However [illegible] vapor pressure [illegible] of the [illegible] temperature [illegible].

[illegible] temperature [illegible] the temperatures are measured [illegible] to determine the gradients [illegible] because only one thermocouple [illegible]. Since the pressure [illegible] constant [illegible] temperature [illegible] have been [illegible] the value [illegible] a precision of 3%.

(22)

The value of α can be determined from liquid density data. In the next chapter it will be shown that the molar volume of liquids can be correlated by the equation

$$\frac{1}{V^2} = A - BT \qquad (40)$$

where V = Molar volume

A, B = Constants

From this equation one finds that

$$\alpha = \frac{B}{2(A - BT)} \qquad (41)$$

From liquid density data for CF_4 cited by Rossi (21) and Fiske (37), the constants in this equation were determined to be

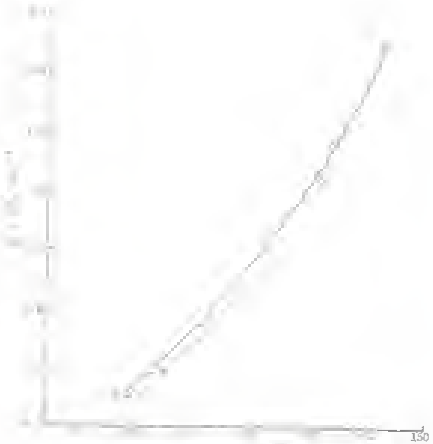
$$A = 4.302 \times 10^{-4} \left(\frac{mole}{cc}\right)^2$$

$$B = 2.0159 \times 10^{-6} \frac{mole^2}{cc^2 \times {}^\circ K}$$

These values of α can be used with the observed values of $\Delta P/\Delta T$ to estimate β, which is needed to make the corrections to $\Delta P/\Delta T$ for thermal expansion of the cell. After corrected values of $(\partial P/\partial T)_V$ have been obtained they can be used with the values of α to calculate more accurate values of β. The results of these measurements and calculations are given in Table 25 and in Figures 32 and 33.

In Figure 32 the thermal pressure coefficient of CF_4 is shown and the curve through the points was drawn by eye as being the best representation of the data. There are three points that deviate noticeably from the curve and were given no weight in drawing the curve. Measurement 1


140
150


150

[illegible] was made before the CF_4 sample had been fully purified. In addition, the threaded connection on the pressure cell was leaking quite badly and a stream of warm helium was continuously blowing through the cell. This leak was subsequently eliminated. Either of these could have caused the measurement to deviate. The other two points that deviate were made on a single sample of CF_4 that was left in the sample well for both measurements 3 and 4. The most likely reasons for these deviations is that some carbon dioxide was condensed into the cell with the sample and dissolved in the liquid. Whether this is true or not, the other data points are consistent enough so that it does not seem reasonable that the curve should be displaced because of measurements made on a single sample. Even these points which were given no weight lie within 5 percent of the curve drawn.

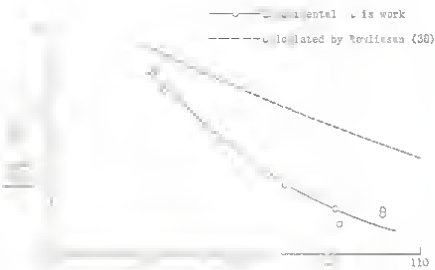
The results of these measurements will be discussed further in later chapters.

CH_4

Direct experimental measurements of the thermal pressure coefficient of CH_4 were not available. No measurements were made in the present work. The rates of temperature rise, temperature gradients, and procedure were the same as for CF_4.

Phillips Research Grade methane was used for these experiments and was 99.60 percent pure as supplied. Traces of air and carbon dioxide were removed by distillation between traps in a glass vacuum system.

The results of these measurements of $(\partial P/\partial T)_V$ for CH_4 are given in Table 26 and in Figure 34. The raw experimental data was given in Appendix C.


θ
110

The liquid compressibility can be calculated from velocity of sound, heat capacity and density data for a liquid. Combining the liquid compressibility and the coefficient of thermal expansion yields the thermal pressure coefficient. Rowlinson (36), in his tables, gives values of the thermal pressure coefficient calculated in this manner, and these values are shown in Figure 34. It can be seen that there is considerable difference between the direct measurements of this work and the indirect values cited by Rowlinson. At higher temperatures this difference amounts to about 15 percent. Because of the number of different quantities to be determined for the indirect method, the direct measurements in the present work are preferred.

There is one other factor in the measurements of the present work which should be mentioned. There was a small leak in the apparatus that was eventually found to be a defect in the convolutions of the nickel bellows. The leak rate was about 7×10^{-6} moles of helium per hour with 1 atm pressure difference across the bellows. This leak rate probably would be smaller with other gases. Since the pressure difference across the bellows is always small during operation of the apparatus, there should be little or no effect by this leak. The bellows were in a compressed condition most of the time during a measurement so that if there were any net flow, helium would be forced into the cell. If helium were forced into the cell, it would either form a bubble or go into solution. If a bubble were formed, the value of $(\partial P/\partial T)_V$ would be that of a gas and would be much lower than the values observed. Helium is not very soluble in liquids at the temperatures used in these measurements, and if it were, it would cause the measured values of $(\partial P/\partial T)_V$ to be high. This leak was present when the measurements here

made for CCl_4, and the good results obtained indicated that the lea
contributed nothing to the experimental error.

CHAPTER VII

THE SMOOTHED POTENTIAL CELL MODEL OF THE LIQUID STATE

There have been several models of the liquid state that have been used to correlate and calculate physical and thermodynamic properties of liquids. Most of these models are quite complex and can only be handled adequately by numerical means. The end results of these labors have not been especially gratifying, and because of the difficulty in using these complex models this author does not consider them to be appropriate for the present work.

Therefore, the model that will be applied to the liquid state in this chapter is simpler than the type mentioned above and can be handled without the use of an electronic computer. Of course, this ease of computation is accomplished at some expense in accuracy of the calculations. Calculations in this chapter will show the model to be qualitatively correct for portions of the liquid state, but as with most of the other liquid-state models, the quantitative agreement with real liquids is not good.

The cell model of the liquid state uses the assumption that each molecule of the liquid is confined by its nearest neighbors to a small cell that is on the order of the molecular size. The force field acting upon each molecule is rapidly fluctuating because of molecular motion and can be replaced by a field of spherical symmetry. The simple cell model does not take account of the fact that for real liquids the

[redacted] exchange places with a frequency that increases with the [redacted] molecule. Thus, the simple cell model cannot be used for the calculation of transport properties. If the average length of time a molecule spends in a cell is sufficiently long, this changing of places will have little effect upon the thermodynamic properties. The cell model gives more order to the liquid state than is actually present, but this error is not as important at low temperatures and high density as it is in the critical region where the cell models give poor agreement with real materials. For this reason, the cell model was not applied to liquids in the region of the critical point in the present work. There are several versions of the cell model which are discussed by Hirschfelder, Curtiss and Bird (1), and by Prigogine (2). Further discussion in the present work will be limited to the smoothed potential cell model, as presented by Prigogine.

The smoothed potential cell model is based on the assumption that the average potential energy of interaction of a molecule in a cell can be replaced by the value of the potential energy when all molecules are at the centers of their cells. The potential energy of the molecule at all positions within the cell is assumed to be equal to this average value, and the molecule is not permitted to move outside the cell. In order to present these assumptions more clearly, it is necessary to define them mathematically. The symbols used are

r = Distance of the molecule from the center of its cell

w(r) = Potential energy of interaction of a molecule with its neighbors as a function of its distance from the center of the cell (expressed as energy per molecule)

w(0) = Potential energy when the molecule is at the center of the cell

d = Average distance between centers of molecules in the liquid

R_0 = Value of r at which the mutual pair potential energy of two molecules is zero

In terms of these variables and parameters, the potential energy of interaction of a molecule in its cell as used in the smoothed potential cell model is

$$\begin{aligned} w(r) - w(0) &= 0 && 0 \le r \le (d - R_0) \\ w(r) - w(0) &= \infty && (d - R_0) \le r \end{aligned} \qquad (42)$$

If the mutual pair potential energy function for a pair of molecules is given by an n-m potential energy function as in Equation 2 then the following equations for the thermodynamic functions apply. The derivation of these equations parallels that of Prigogine for the 6-12 potential and is not given here.

$$R_0 = \frac{NzE^*}{2\left[1-\frac{m}{n}\right]}\left[C\left(\frac{v^*}{v}\right)^{n/3} - \frac{D}{2}\left(\frac{v^*}{v}\right)^{m/3}\right] \qquad (43)$$

$$P = \frac{-zE^*m}{6\left[\frac{n}{m}-1\right]v}\left[C\left(\frac{v^*}{v}\right)^{n/3} - \frac{D}{2}\left(\frac{v^*}{v}\right)^{m/3}\right] + \frac{kT}{v}\left[1 - \frac{1}{8}\left(\frac{v^*}{v}\right)^{1/3}\right]^{-1} \qquad (44)$$

where N = Total number of molecules considered

z = Number of nearest neighbors to a molecule

E^* = Potential energy function parameter from mutual pair potential energy function for two isolated molecules

v = Volume per molecule

v^* = Volume per molecule when the average separation between molecules is equal to R^*

a = Ratio of R^* to R_0, where R^* is the separation at the minimum in the isolated pair mutual potential energy function and R_0 is the separation at which this potential energy is zero. Equation 3 can be used to determine a if r_0 and r^* are replaced by R_0 and R^*, respectively

E_0 = Configurational energy of N molecules relative to an energy zero at infinite separation of the molecules

P = Absolute pressure

T = Absolute temperature

C,D = Geometric constants which take non-nearest neighbor interactions account. If non-nearest neighbor interactions are neglected $C = 1.0$ and $D = 2.0$

In order to determine the constants C and D, a lattice structure for the liquid must be assumed. The lattice usually used to determine these constants is the face-centered cubic lattice. For this lattice and the 6-12 potential these constants are (1,2)

$C = 1.01$

$D = 2.41$

For this lattice and the 7-28 potential, the constants are (39)

$C = 1.00$

$D = 2.226$

These constants will be used in further calculations involving these potentials.

Molar Volume of Liquids

At vanishing external pressure the equation of state for a liquid (Equation 44) reduces to the following

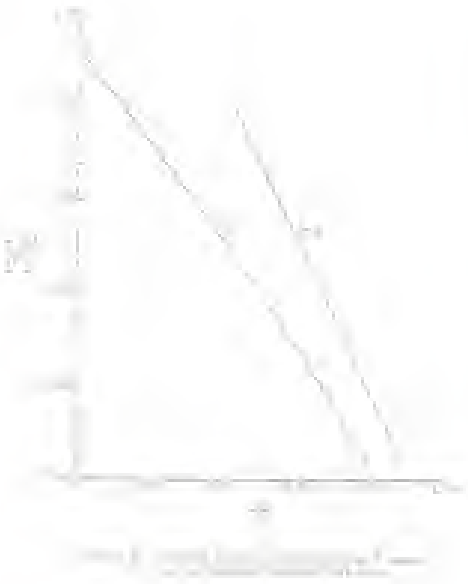
$$\frac{kT}{\epsilon E^{*}} = \frac{n}{4\left(\frac{n}{3}-1\right)}\left[C\left(\frac{v^{*}}{v}\right)^{n/3} - \frac{D}{2}\left(\frac{v^{*}}{v}\right)^{m/3}\right]\left[1 - \frac{1}{6}\left(\frac{v^{*}}{v}\right)^{1/3}\right] \qquad (45)$$

From this equation of state when $T = 0$,

$$\left(\frac{v^{*}}{v}\right)_{T=0} = \left(\frac{D}{2C}\right)^{\frac{3}{n-m}} \qquad (45)$$

Thermimum, from this equation of state the volume per molecule at absolute zero is slightly smaller than the volume when the average separation is equal to E^{*}. Only when near-nearest neighbor interactions are neglected does the volume at absolute zero equal v^{*}.

Reed (21) found that the more complex Lennard-Jones Devonshire equation of state for the 6-12 potential predicted that a plot of $1/v^{2}$ against temperature should be linear. (V is the molar volume of the liquid.) Equation 45 cannot be solved explicitly for $1/v^{2}$, and it cannot be seen by inspection that the equation of state from the smoothed potential cell model predicts this. One can, however calculate numerically the values $kT/\epsilon E^{*}$ that corresponds to given v/v^{*} values and plot these values to determine whether this model predicts that $1/V^{2}$ vs. T should plot linearly. This was done for the 6-12 and 7-28 potentials and the results are shown in Figure 35. In this figure it can be seen that the plot is exactly straight for the 6-12 potential and that it curves slightly for the 7-28 potential. The curvature for the 7-28 potential is so slight that it would be undetectable over the range of temperatures usually covered by most liquids up to their normal boiling points. Thus, according to this model the plots of $1/V^{2}$ against T should be very nearly linear for molecules that have very narrow



otential energy functions as in the 7-28 potential as well as for molecules that follow the 6-12 potential

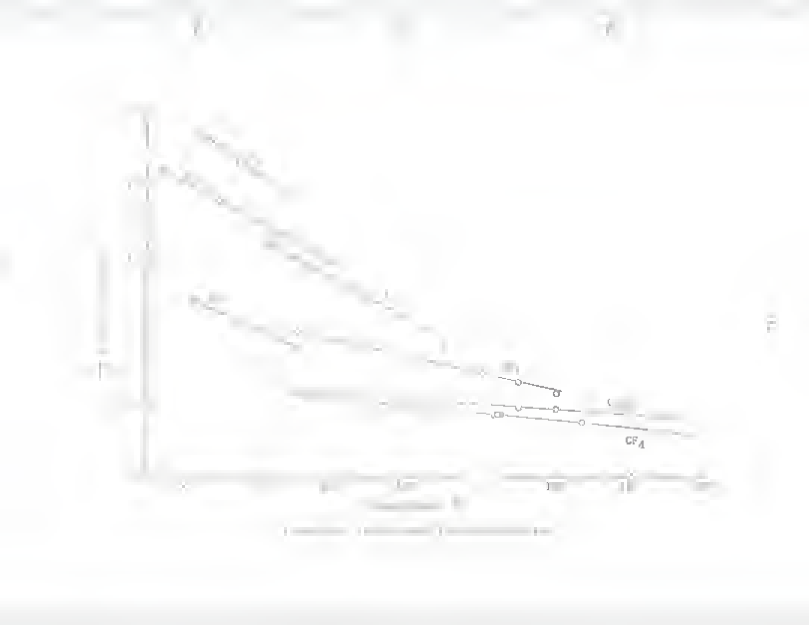
In Figures 36 and 37 $1/V^2$ is plotted against T using experimental values of the molar volume The data used in the figures were taken from the references given below

Molecule	Reference
A, N_2, O_2, CH_4, CCl_4	38
F_2	21
$C(CH_3)_4$	28
CF_4	21 37
C_2H_6	20

Those data may be seen to give very straight lines except for some curvature at high temperatures where the assumptions of the cell model are not as good as at lower temperatures. Values of the constants A and B in Equation 40 were evaluated for the compounds shown in Figures 36 and 37. These values as well as the extrapolated molar volumes at absolute zero temperature, are given in Table 27

The extrapolated values of the molar volumes of the supercooled liquids at absolute zero (V^0) are in very good agreement with the values calculated by Kurtz (40) for hydrocarbons using other extrapolation methods For CH_4, Kurtz gave the value 28 0 cc /mole which compares favorably with the value 28 89 from the present work For C_2H_6, Kurtz gave the value 42.0 cc./mole compared to the value 40 33 from the present work For n-C_5H_{12} and i-C_5H_{12} Kurtz gave 84 1 cc./mole while the value for $C(CH_3)_4$ in the present work was 83 6 cc /mole

From Equation 46, one would expect that the volume per molecule in the supercooled liquid state would be slightly smaller than v^* The


CF_A

smoothed potential cell model does not take into account the fact that the molecular vibrations at absolute zero will cause some addition to the volume at absolute zero over what is shown in Equation 46. Even if these vibrations are not taken into account, the value of v^*/v at 0°K is only 1.092 for the 6-12 potential, which makes $R^*/d = 1.03$ at 0°K. For the 7-28 potential at absolute zero, Equation 45 gives $v^*/v = 1.031$ and $R^*/d = 1.01$. Therefore, the molecular separation at absolute zero should give estimates of R^* that are low by a maximum of 3 percent. For close packing of spherical molecules at absolute zero, the molecular separation is (1.8)

$$R^* = 1.329(v^0)^{1/3} \qquad (47)$$

where R^* is in angstroms and the molar volume at absolute zero, v^0, is in cubic centimeters per mole. Values of R^* determined from Equation 47 are given in Table 27 for many of the molecules for which calculations were made in Part I. Also given in Table 27 are empirical R^* values for the 6-12 potential taken from References 1 and 21. Values of R^* calculated for these molecules in Part I are also given in this table for comparison. It can be seen that, in general, the values of R^* from Equation 47 are smaller than both the 6-12 potential values from experimental data and the calculated values from Part I. The calculated values from Part I were generally lower than the 6-12 values and are in better agreement with the R^* values from Equation 47. These results indicate that the calculations in Part I may have given R^* values that are slightly larger than the true R^* values for these molecules.

Better agreement with the R^* values from the molar volume data probably could have been obtained in some cases by empirically fitting to experimental second virial coefficient data R^* and E^* values for the

[illegible] potential energy functions from Part I. When this was done for CCl_4 the value $R^0 = 6.70$ A was obtained which is in better agreement with the value 6.54 A from molar volume data

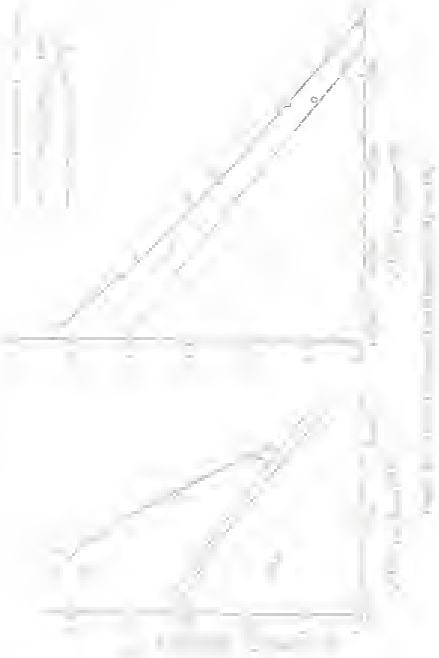
Thermal Pressure Coefficient of Liquids

The thermal pressure coefficient for the smoothed potential cell model can be determined by partial differentiation of Equation 44 to be

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{k}{v}\left[1 - \frac{1}{6}\left(\frac{v_0}{v}\right)^{m/3}\right]^{-1} \qquad (47)$$

It is interesting to note from this equation that the only dependence of $(\partial P/\partial T)_V$ upon the exponents m and n in an m-n potential comes in the parameter e which is not strongly sensitive to changes in m and n. Rearrangement of this equation shows that a plot of $\left[V(\partial P/\partial T)_V\right]^{-1}$ against $V^{-1/3}$ should be a straight line with slope $-(V^*)^{1/3}/Nk$e and intercept $1/Nk$e. Note that V^*/σ^3 represents the molar volume of the liquid when the average separation of the molecules is equal to R_0. The value of $(V^*)^{1/3}/e$ should be less than the cube root of the molar volume at absolute zero, but of the same order of magnitude. (For the 6-12 potential e = 1.122σ and for the 7-28 potential e = 1.0683σ.)

In Figures 38, 39 and 40, thermal pressure coefficient data for A, O_2, N_2, CCl_4, CH_4 and CF_4 are plotted as described above. The data for A, N_2, O_2, CCl_4 and a curve for CH_4 were taken from the tables of Rowlinson (38). The other values of $(\partial P/\partial T)_V$ for CH_4 and the values for CF_4 are the values determined experimentally in the present work. There is some curvature in the lines drawn through the points in these figures but the slopes do not change rapidly. Since there is some curvature in the lines on the figures, values of $(V^*)^{1/3}$ cannot be



determined from these plots. It is interesting, however, to see if the slopes of the curves are of the order of magnitude that would be expected if the volumes of the supercooled liquids at absolute zero were used in place of $V^*/\sqrt{3}$. The volumes corresponding to V^*, V^0 and $V^*/\sqrt{3}$ are in the order $V^0/\sqrt{3}<V^*<V^*$. Straight lines with slopes $-(V^0)^{1/3}/Nk$ are shown for comparison in these figures. (These slopes are slightly larger in absolute value than they would be if $V^*/\sqrt{3}$ had been used.) The intercepts of the actual curves were larger than $1/Nk$, and the dashed lines of constant slope were arbitrarily positioned on the ordinate for easy comparison of slopes.

The values of the thermal pressure coefficient of argon in Rowlinson's tables is a combination of direct measurements above 90°K and values below 90°K calculated from velocity of sound data. These values from the two sources appear to be about 10 percent apart, with the calculated values higher. Rowlinson used the values from direct measurement at higher temperatures and drew a smooth curve to connect with the values calculated from the velocity of sound at lower temperatures. This makes the value of the thermal pressure coefficient change rapidly with temperature at the lower temperatures in the tables of Rowlinson. The slope of the curve in Figure 38 for the direct measurements is in much better agreement with the slope $-(V^0)^{1/3}/Nk$ than for the curve taken from Rowlinson's tables.

With this explanation of the curve for argon, the slopes of the curves from experimental and calculated thermal pressure coefficients given in Figures 38, 39, and 40 are in good agreement with the slopes taken from the liquid molar volume at absolute zero temperature. The curve from the experimental measurements of the present work for CH_4 is

an exception to this agreement. In view of the good agreement between the actual slopes and the slopes from V^0 for all the other compounds considered (even the direct measurements for CF_4 from the present work) it appears that additional measurements for CF_4 might be advisable.

x for Liquids

Another quantity that can be calculated from the smoothed potential cell model is x which is defined as

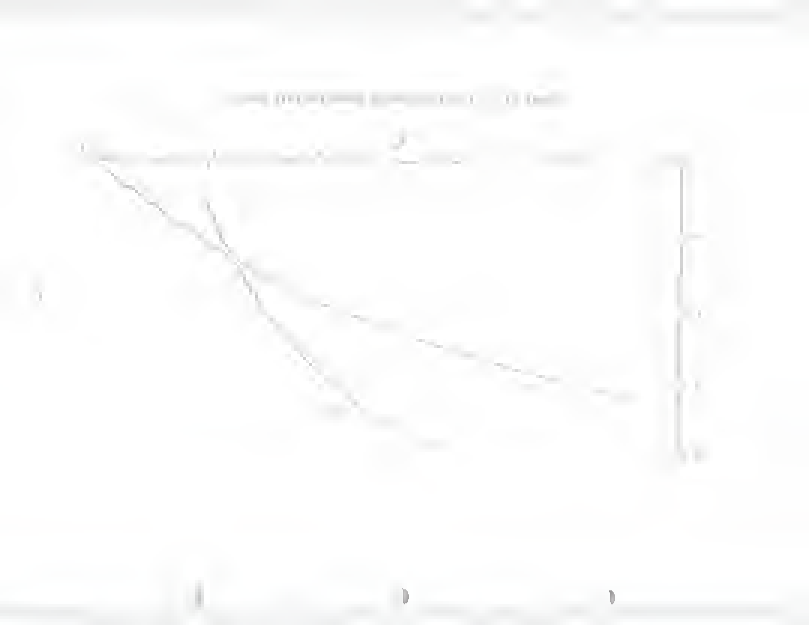
$$x = \frac{-(\partial E_c/\partial V)_T}{E_c/V} \tag{49}$$

By differentiating Equation 43 for the smoothed potential cell model, x is found to be given by

$$x = \frac{\frac{1}{3}\left[6\left(\frac{v^*}{v}\right)^{n/3} - \frac{n}{2}\left(\frac{v^*}{v}\right)^{n/3}\right]}{\left[\left(\frac{v^*}{v}\right)^{n/3} - \frac{n}{2m}\left(\frac{v^*}{v}\right)^{m/3}\right]} \tag{50}$$

Values of x at several values of v^*/v were calculated for the 6-12 and the 7-28 potentials and these values were plotted to give the curves in Figure 41. These curves show that over the range of v^*/v normally occurring in the liquid ($0.6 < v^*/v < 0.9$) state, the value of x should be larger for substances which follow the 7-28 potential than for those that follow the 6-12 potential. It is probably true that x becomes larger at a given value of v^*/v as the reduced potential energy function becomes narrower (as n and m increase).

The value of x for real substances can be determined from Equation 49, but this is not the most accurate method of calculation since most configurational energy data is determined from vapor pressure data. To calculate $(\partial E_c/\partial V)_T$ would amount to differentiating the experimental



vapor pressure data twice. Few data are accurate enough to retain very much accuracy after two differentiations.

Another method of evaluating x involves using the thermal pressure coefficient to determine $(\partial E_c/\partial V)_T$. From thermodynamics

$$\left(\frac{\partial E_c}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (51)$$

Since for most liquids below their boiling points P is small compared to $T(\partial P/\partial T)_V$

$$\left(\frac{\partial E_c}{\partial V}\right)_T \cong T\left(\frac{\partial P}{\partial T}\right)_V \qquad (52)$$

Thus

$$x \cong \frac{-T\left(\frac{\partial P}{\partial T}\right)_V}{E_c/V} \qquad (53)$$

The configurational energy, E_c, is the energy of the liquid relative to the ideal gas at the same temperature. Values of x for A, N_2, O_2, and CH_4 can be calculated from the tables of Rowlinson (58). Values of x can also be calculated for CH_4 from the values of $(\partial P/\partial T)_V$ measured experimentally in the present work and the configurational energies given by Rowlinson. The configurational energy of CF_4 was calculated from the vapor pressure equation cited by Reed (21), using second virial coefficients to correct for vapor imperfections and the liquid molar volume data presented earlier in this chapter. The configurational energy of CF_4 at its vapor pressure is given in Table 29, and the values of x for CH_4 and CF_4 using the experimental thermal pressure coefficients determined in the present work are given in Table 28. Values of x for CCl_4 are given by Hennings and Scott (30).

It seems reasonable to assume that V^0 can be used to approximate V^* in determining reduced liquid volumes. In Figure 42, x is plotted against V/V^0 for the liquids mentioned above.

The smoothed potential cell model predicts that x should increase with increasing liquid volume, but Figure 42 shows that this is not necessarily so. Since values of x include measurements of E_0, V_l and $(\partial P/\partial T)_V$ when the thermal pressure coefficients are measured directly and ever more measurements when the thermal pressure coefficient is calculated indirectly, x can be determined to better than to within 1 percent. Therefore, too much importance should not be given to the shapes of the curves in Figure 42.

The curves in this figure confirm the prediction from the smoothed potential cell model that at the same value of v/v^* molecules with narrower reduced potential energy functions should have higher values of x. The potential energy functions of CF_4 and CCl_4 are both narrower in reduced coordinates than those for the other materials shown in Figure 42. Hildebrand and Scott (41) give values of x for other nonpolar polyatomic molecules which would be expected to have fairly narrow reduced potential energy functions. Some of these values are

Substance	x
$n\text{-}C_7F_{14}$	1.09
$SiBr_4$	1.04
$SnCl_4$	1.04
$TiCl_4$	1.02
$SiCl_4$	1.09
Benzene	1.05

These values, being relatively high, are in agreement with the

conclusions given above regarding the shape of the potential energy functions.

The theoretical significance of x is somewhat nebulous. The equation of state of van der Waals predicts that x should be unity, so that x can be regarded as a measure of the deviation of the real fluid from a van der Waals' fluid. Since the total range of x values was from about 0.8 to about 1.1, van der Waals' equation of state should come fairly close to fitting configurational energies for the liquid state.

The calculations in this chapter have shown that the smoothed potential cell model gives good qualitative predictions about the liquid state. These calculations have not revealed much information about the potential energy functions of the molecules, however. For example, it was found that the molar volumes of liquids can be correlated by the same type of equation, regardless of the potential energy function, and the same was found to be true for the thermal pressure coefficient. The value of x, however, did give some indication of the width of the reduced potential energy function, and the prediction of the smoothed potential cell model that x should be larger for molecules with narrower wells in their reduced potential energy functions was found to be correct.

CHAPTER VIII

CONFIGURATIONAL ENERGY-VOLUME RELATIONSHIP IN LIQUIDS

The distribution of computer molecules about a given molecule in a [illegible] will on the average be spherically symmetrical. If we select a differential volume element $d\tau$ at a distance R from the given molecule, then the probability of finding a molecule in this volume element is $N_V g(R) d\tau$, where N_V is the average number of molecules per unit volume, and g(R) is the radial distribution function which describes the density variations in the liquid. Actually, the radial distribution function is also dependent upon the molar volume and the temperature so that it is proper to write the radial distribution function as $g(R,V,T)$.

In terms of the radial distribution function, the configurational energy of the liquid is given by (7,41)

$$E_c = \frac{2\pi N^2}{V} \int_0^\infty U(R) g(R\ V\ T) R^2 dR \qquad (54)$$

If one assumes that the mutual pair potential energy function is of the Lennard-Jones n-m type, then actually U(R) is a function of R^* and R/R^* and one may use

$$U(R) = R^* U_1\left[\frac{R}{R^*}\right] \qquad (55)$$

as a general form of this type of potential. Also, it has frequently been assumed that g(R,V,T) depends only upon the potential energy

mation and size and energy parameters for the molecules of the fluid so that we could then just as well write

$$g(R, V, T) = g_1(y, V/R^{*3}, T^*) \qquad (55)$$

where $y = R/R^*$

$T^* = kT/\epsilon^*$

Making these substitutions in Equation 54, and changing the variable of integration from R to y gives

$$\frac{E_0 V}{N^2 \epsilon^* R^{*3}} = 2\pi \int_0^\infty U_1(y) g_1(y, \frac{V}{R^{*3}}, T^*) y^2 dy \qquad (57)$$

Since the equation of state of a liquid is dependent only upon the potential energy function of the molecules, the molar volume along the saturation curve of a liquid can be expressed in terms of T^*. The right-hand side of Equation 57 is thus actually a function only of T^* along the saturation curve. The left-hand side of Equation 57 is the negative of the reduced van der Waals' $a = -a^*$. From Equation 57, one can determine that for molecules which have the same form of potential energy function (same values of n and c), plots of a^* against T^* should give a single curve. One would not necessarily expect that ϵ^* would be the same for molecules which have potential energy functions of different shapes, however.

In the derivation of Hildebrand and Wood (41, 42) which is used in developing Hildebrand's theory of solutions, the assumption is made that ϵ^* is the same for all substances. Since this is an important point in the theory, it is desirable to see if ϵ^* is really the same for all substances, regardless of potential energy functions.

Configurational energy values for A, N_2, D_2, CH_4, and CCl_4 can be calculated from the tables of Rowlinson (38). Calculations of configurational energies for other compounds were made in the present work as described below.

CF_4. An equation for the vapor pressure of CF_4 is cited by Reed (21), and heat of vaporization values were calculated from this equation using the Clapeyron equation. The configurational energy was then calculated using Pitzer's correlation (10) to determine the enthalpy difference between the real and ideal gases and to correct the vapor volume. The liquid molar volume was calculated from the equation presented in the previous chapter.

C_2N_2. The enthalpy of the ideal gas over a portion of the liquid range and the heat of vaporization over the entire liquid range are given by Din (20). Also given are the liquid volumes over the liquid range. Pitzer's correlation was used to calculate the difference between real and ideal-gas enthalpy for the temperatures at which no data were given. These data were sufficient to calculate E_c.

C_2F_6. Reed (21) cites two values of the enthalpy of vaporization of C_2F_6 at its normal boiling point and the liquid volume at the normal boiling point. Pitzer's correlation was used to calculate the difference between real and ideal-gas enthalpy.

$C(CH_3)_4$. The heat of vaporization at two temperatures and the liquid molar volume are given in Reference 28. Pitzer's correlation was used to calculate the difference between real and ideal-gas enthalpy.

[illegible] configurational energy and molar volumes [illegible] are given in Table 29

[illegible] is plotted against T^* for the [illegible] using 6-12 potential parameters for E^* and R^*. The parameters used for this figure are given in Table 30. For the molecules A, N_2, O_2, CH_4, and C_2H_6, which come fairly close to fitting the 6-12 potential, the value of σ^* is reasonably close to the same (about a 10 percent range) at a given T^*. For the molecules CF_4, C_2F_6, CCl_4, and $C(CH_3)_4$, which were shown in Part I to have potential energy functions that were very much different from a 6-12 potential, the value of σ^* is very much different.

Since all of the molecules above, even the diatomic gases, do not follow the 6-12 potential, the wide range in the values of σ^* might be thought to occur because of this. In Figure 44, σ^* is plotted against T^*, but this time the potential energy function parameters used were the E^* and R^* values calculated in Part I which gave the best agreement with experimental second virial coefficient data. The values used are given in Table 30. Use of these parameters caused the values of σ^* for the various compounds to have just as wide a range as when the 6-12 parameters were used. Although the calculated potential energy function parameters may not be the best for each molecule, they are not in error enough to cause the wide variation in the value of σ^*.

It is apparent, therefore, that the value of σ^* is different for molecules which have different shapes of potential energy functions. The Hildebrand theory of solutions should, as suggested by Reed (44), be modified to take the difference in the values of σ^* into account. Since σ^* is evidently dependent upon the shape of the potential energy

function, an additional parameter that takes the shape of the potential energy function into account (such as Pitzer's ω) might possibly be used to make an improvement in the Hildebrand theory.

SUMMARY OF PART II

In Chapter VI, measurements of the thermal pressure coefficient of CCl_4 CF_4, and CH_4 were described and the results were presented. The results for CCl_4 agree with other published experimental measurements but the results for CH_4 are in poor agreement with values calculated from velocity of sound data. The experimental results of the present work are preferred for CH_4. No other measurements are available for comparison with the results in the present work for CF_4.

The smoothed potential well model was applied to the liquid state and it was predicted that plots of $1/V^2$ (V = molar volume) against temperature should be approximately linear for all liquids. This was found to be true, and from plots of experimental molar volumes the volume, V^0, of the supercooled liquid at absolute zero temperature was determined for several compounds. These extrapolated volumes at absolute zero were used to estimate values of R^* for the substances considered. Values of R^* calculated from V^0 were generally smaller than R^* values obtained empirically for the 6-12 potential and smaller than the R^0 values for the more realistic potentials calculated in Part I. The R^*'s calculated in Part I are smaller than the 6-12 R^*'s and are in better agreement with the R^*'s at absolute zero temperature. The R^*'s calculated from V^0 values should be smaller than R^0's from the calculations of Part I by up to 3 percent, but the actual difference is larger

than this. These results indicate that the calculated values of R^0 from Part I might be slightly larger than the actual R^0's for the molecules.

With the smoothed potential cell model, it was found that the thermal pressure coefficient should also be insensitive to changes in potential energy functions, and that plots of $\left[V(\partial^2 P/\partial T^2)_V\right]^{-1}$ against $V^{-1/3}$ should be linear. These plots were made for several substances, and some curvature was found. The slopes of these curves were found to be in good agreement with what would be expected from the smoothed potential cell model based upon the molar volume of the compounds at absolute zero temperature.

The smoothed potential cell model also predicted that the value of $-(\partial E/\partial V)_T / E/V$ should be larger for molecules which have narrower wells in the reduced potential energy function. This was found to be true for real substances.

In Chapter VIII, it was shown that the value of the reduced van der Waals' $a = a^0$ is not the same for all molecules, but depends upon the shape of the potential energy function. This finding suggests that a reexamination should be made of the Hildebrand theory of solutions which assumes that a^0 is the same for all substances.

Although the calculations in Part II are interesting, they give little quantitative information about the potential energy functions of the molecules studied. The results of Part I regarding the shapes of the potential energy functions are supported by the results of Part II. It was also found that the smoothed potential cell model gives very good qualitative predictions for the liquid state.

TABLE I

REDUCED SECOND VIRIAL COEFFICIENTS FOR n-6 POTENTIALS

6-12 Potential		6-18 Potential		6-24 Potential	
T^*	B^*	T^*	B^*	T^*	B^*
4.0	0.1154	3.63	0.2581	3.40	0.3261
3.5	+0.0190	3.04	0.1425	2.84	0.2153
3.0	-0.1152	2.60	+0.0141	2.432	+0.0943
2.5	-0.3125	1.978	-0.2803	2.112	-0.0369
2.0	-0.6276	1.414	-0.8261	1.838	-0.3300
1.5	-1.2009	0.919	-2.0584	1.232	-0.8511
1.0	-2.5381			0.839	-1.9772
0.8	-3.7342				
0.7	-4.7100				

7-14 Potential		7-21 Potential		7-28 Potential	
T^*	B^*	T^*	B^*	T^*	B^*
4.000	0.3562	3.04	0.2547	3.9635	0.5446
2.778	+0.1177	2.40	0.2610	3.1745	0.4590
2.367	0.0177	1.978	+0.0444	2.422	0.3199
1.778	-0.3459	1.414	-0.3596	1.7638	+0.0843
1.000	-1.598	0.919	-1.257	1.4631	-0.1807
		0.500	-4.7161	1.0533	-0.5679
				0.7937	-1.4252
				0.6350	-2.3529
				0.5291	-3.4948
				0.4535	-4.918

TABLE 2

REDUCED BOYLE TEMPERATURES FOR n-n POTENTIALS

Potential	$T_B^* = \frac{kT_B}{\epsilon}$	$\frac{\epsilon^*_{n-n}}{\epsilon^*_{6-12}}$
7-∞	0 94	3 63
7-28	1 65	2 07
7-21	1 90	1 79
7-14	2 41	1 42
6-∞	1 17	2 92
6-24	2 19	1 56
6-18	2 56	1 33
6-12	3.41	1 00

TABLE 3

[illegible] PARAMETERS FROM SECOND VIRIAL COEFFICIENTS (3)

[illegible]	6-12			7-28		$\frac{(\varepsilon^* r^{*})_{7-28}}{(\varepsilon^* r^{*})_{6-12}}$	$\frac{\varepsilon^*_{7-28}}{\varepsilon^*_{6-12}}$
	ε^*/k °K	r^* Å		ε^*/k	r^*		
[illegible]	119 7	3 83		240	3 36	1 74	2 01
[illegible]	172 7	4 03		340	3 48	1 70	1 97
[illegible]	224 5	4 56		470	3 88	1 78	2 09
N_2	95 0	4 15		190	3 64	1 76	2 00
O_2	118	3 89		240	3 42	1 79	2 03
CO	102	4 24		200	3 69	1 70	1 95
CH_4	148 2	4 28		310	3 63	1 77	2 09
CF_4	153	5 29		3 [illegible]	4 63	1 80	2 06
SiF_4	149	5 28		331	5 03	1 75	2 22
SF_6	189	5 65		414	5 37	1 77	2 19
$C(CH_3)_4$	236	6 25		561	6 09	1 82	2 46
			Average			1 77	2 10

[illegible]	[illegible]	Bond Length, Å
N_2	[illegible]	0.7415
O_2	[illegible]	1.0976
O_2	[illegible]	1.20741
[illegible]	[illegible]	1.418
Cl_2	[illegible]	1.988
C_2H_6	[illegible]	1.536
CF_4	[illegible]	1.323
C_2F_6	[illegible]	1.54
	[illegible]	334
CCl_4	[illegible]	1.76
SF_6	[illegible]	[illegible]
SiF_4	Si – F	1.561
$C(CH_3)_4$	C – C	1.541
$C_2(CH_3)_6$	C – C	1.541
	$C - CH_3$	1.541
$Si(CH_3)_4$	Si – C	1.909
CH_4	C – H	1.0910

TABLE 5

[illegible] OF THE 6-12 POTENTIAL (1)

Gas	$\mathcal{E}^{o}/\kappa$ °K	r_{e} Å	r^{*} Å
He	10 22	2 576	
	10 22	2 556	
Average	10 22	2 566	2 85
Ne	35 7	2 789	
	35 6	2 749	
	34 9	2 78	
Average	35 4	2 773	3 11
A	124	3 418	
	116	3 405	
	119 8	3 405	
	122	3 40	
Average	120	3 422	3 84

[illegible] IN CALCULATING POTENTIAL ENERGY FUNCTIONS OF DIATOMIC GASES

Molecule	α	ρ	r^*/ρ	r^*_0
F_2	2 85	0 371	7 76	4 25
N_2	3.11	0 549	5 56	3 29
O_2	3.11	0 604	5.15	3 07
F_2	3 11	0 709	4 39	2 74
Cl_2	3 84	0 994	3 85	2 52

TABLE I

SUMMARY OF POTENTIAL ENERGY FUNCTION CALCULATIONS FOR DI-TO-IC [illegible]

Molecule	Experimental 6-12 Molecular Parameters (a)		Exponents for Best m-n Fit		Molecular To Atomic Parameter Ratio	Single Atom Energy Parameter	Calc. [illegible] Dis[illegible] Par[illegible] C[illegible]
	$\frac{\epsilon^*_{6-12}}{k}$ °K	$R^*_{6\ 12}$ Å	m	n	$\frac{\epsilon^*_{m-n}}{\epsilon^*_{6-12}}$	ϵ^*/k °K	
H_2	37 0	3 28	6	14	2 34	14 2	3 15
	33 0	3 34					
	38 0	3 27					
Average	36 0	3 29					
N_2	91 5	4 13			2 24		3 61
	95 05	4 15					
	95 5	4 17					
Average	94 1	4 15					
D_2	114	3 85			2 04		3 70
	117 5	4 02					
	118	3 85					
Average	116	3 92					

TABLE 7 (Continued)

Molecule	Experimental 6-12 Molecular Parameters (a)		Exponents for Best m-n Fit		Molecular To Atomic Parameter Ratio	Single Atom Energy Parameter	Calculated Distance Para For Min
	$\frac{\epsilon^*_{6-12}}{k}$ °K	R^*_{6-12} A	m	n	$\frac{R^*_{m-n}}{\xi R^*}$	ϵ^*/k °	[illegible]
F_2	121 (b)	4 05	6	18	1 70	90 7	[illegible]
	112	3 78					
Average	114	3 91					
Cl_2	357	4 [illegible]	6	21	1 43	365	3 00
	257	4 01					
Average	307	4 12					

(a) Data taken from Hirschfelder, Curtiss Bird (1) [illegible] otherwise noted

(b) All experimental parameters for F_2 obtained by [illegible] and Firmack (12)

TABLE 8

POTENTIAL ENERGY FUNCTION OF H_2

R	U/E*	R/R*	U/E*
1.4921	-0.1987	1.0478	-0.9311
1.4653	-0.1744	1.0317	-0.9650
1.4284	-0.1954	1.0197	-0.9890
1.3858	-0.2242	1.0000	-1.0000
1.3551	-0.2583	0.9541	-0.9858
1.3333	-0.2955	0.9383	-0.9423
1.3216	-0.3356	0.9324	-0.8549
1.3098	-0.3883	0.9265	-0.7083
1.2981	-0.4455	0.9206	-0.4722
1.2863	-0.5110	0.9048	-0.1198
1.2746	-0.5856	0.8889	+0.3956
1.2629	-0.6674	0.8730	1.1400
1.2511	-0.7543	0.8571	2.1981
1.0794	-0.8475	0.8413	3.6957
1.0635	-0.8710		

TABLE 9

POTENTIAL ENERGY FUNCTION OF N_2

	U/ε^*	$R/\mathring{A}^*$	U/ε^*
	-0.4409	1.0725	-0.8611
	-0.1814	1.0810	-0.9265
	-0.2355	1.0895	-0.9569
17	-0.3032	1.0981	-0.9758
92	-0.3917	0.9867	-0.9848
2698	-0.4678	0.9652	-0.9899
37	-0.5165	0.9438	-0.9902
03	-0.6115	0.9223	-0.9812
1.88	-0.8705	0.9009	+0.2397
1.54	-0.7329		
1.0689	-0.7472		

TABLE 10

POTENTIAL ENERGY FUNCTION OF O_2

R	U/E*	R/R*	U/E*
[illegible]	-0.1361	1.0341	-0.9528
[illegible]	-0.1791	1.0131	-0.9913
[illegible]	-0.2378	0.9901	-0.9902
[illegible]	-0.2890	0.9670	-0.9185
[illegible]	-0.2895	0.9440	-0.7245
[illegible]	-0.4752	0.9210	-0.3228
1.12	-0.6208	0.8979	+0.4200
1.202	-0.8[illegible]2		
1.052	-0.7[illegible]1		
1.0021	-0.[illegible]7		
1.0491	-0.[illegible]5		

[illegible]

[illegible] OF F_2

[illegible]	[illegible]	γ/γ^*	U/E^2
[illegible]	[illegible]	1 1340	-0 4523
[illegible]	[illegible]	1 0879	-0 7336
50	[illegible]	1 0822	-0 8123
102	[illegible]	1 0547	-0 8919
2 44	[illegible]	1 0308	-0 9296
37	[illegible]	1 0052	-0 9554
599	[illegible]	0 9794	-0 9685
871	[illegible]	0 9536	-0 9748
2 13	[illegible]	0 9278	-0 4247
1 1856	-0 8401	0 9021	-0 4035
1 1598	-0 5793	0 8763	2 0432

TABLE 12

[illegible] RGY FUNCTION OF Cl_2

		R/R*	U/E*
		1 1200	-0 6634
		1 1000	-0 7474
		1 0800	-0 8131
		1 0600	-0 8777
		1 0400	-0 9355
		1 0200	-0 9815
		1 0000	-1 0000
00		0 9800	-0 9705
00		800	-0 8600
1200		0 [illegible]0	-0 6158
00		0 9[illegible]0	-0 1434
1 1000		00	+0 6902
1 1600	-0 [illegible]	0 0000	2 1462
1 1400	-0 4229		

6-12 POTENTIAL PARAMETERS FOR CH_4

[illegible]	σ_A	ε_0 λ	Sc [illegible]
[illegible]	[illegible]	3 82	1
[illegible]	[illegible]	3 80	[illegible]
[illegible]	148	3 [illegible]	[illegible]
[illegible]	145	3 72	[illegible]
[illegible]	144	3 83	

TABLE 1

[illegible] OF C_2H_6

[illegible]	[illegible]	[illegible]	T^*	D/ε^*
[illegible]	[illegible]	[illegible]	1.2371	-0.1776
[illegible]	[illegible]	[illegible]	3.375	-0.2190
[illegible]	[illegible]	[illegible]	1.3.3	-0.2716
[illegible]	[illegible]	[illegible]	7[illegible]	-0.3383
[illegible]	[illegible]	[illegible]	[illegible]	-0.4220
[illegible]	[illegible]	[illegible]	[illegible]	-0.5285
[illegible]	[illegible]	[illegible]	[illegible]	-0.6571
[illegible]	[illegible]	[illegible]	[illegible]	-0.8036
[illegible]	[illegible]	[illegible]	[illegible]	-0.9434
[illegible]	[illegible]	[illegible]	[illegible]	-1.0338
[illegible]	[illegible]	[illegible]	[illegible]	-1.0959
[illegible]	[illegible]	[illegible]	[illegible]	-1.0495
[illegible]	[illegible]	[illegible]	[illegible]	-1.0265
[illegible]	[illegible]	[illegible]	[illegible]	-1.0416
[illegible]	[illegible]	[illegible]	[illegible]	-1.144

TABLE 15

CRITICAL CONSTANTS AND THE ACENTRIC FACTOR

Substance	ω	T_c, °K	P_c, Atm	Source of Critical Constants
A	−0 002	150 72	48 00	10
CH_4	0 013	190 66	45 795	10
N_2	0 040	126 26	33 540	10
C_2H_6	0 105	305 75	48 864	10
$C(CH_3)_4$	0 195	433 76	31 57	10
Cl_2	0 0741	417 2	76 1	26
F_2	0 057	144	55	21
CF_4	0 189	226	37	21
C_2F_6	0 251	292 9	29 9	21
CCl_4	0 191	556 3	45 0	27
SiF_4	0 364	259 0	36 7	21
$Si(CH_3)_4$	0 227	458	33	27
SF_6	0 208	318 7	37 1	21
$C_2(CH_3)_6$	0 388	545	25 7	28

TABLE 16

CALCULATED PARAMETERS FOR POLYATOMIC MOLECULES

Calculation	r_0^*	E^*/k °K	R^* A
CF_4 - 1	1.90	297 0	4 93
- 2	1.90	271 2	4 93
- 3	1 90	254 5	5 00
C_2F_6 - 1	1 60	342 7	5 81
- 2	1 60	332 2	5 825
- 3	1 60	326 3	5 84
CCl_4 - 1	1 80	702 0	6 44
- 2	1 80	678 9	6 445
- 3	1.80	665 8	6 46
$C(CH_3)_4$ - 1	2.10	480 1	6 38
- 2	2.10	462 4	6 39
- 3	2.10	450 4	6 40
$C_2(CH_3)_6$ - 1	1 85	715 6	7 14
- 2	1 85	683 4	7 16
- 3	1 85	661 8	7 17
SF_6 - 1		594 3	5 45
- 2		475 1	5 49
- 3	1 75	413 0	5 51
SiF_4 - 1	1 90	344 2	5 37
- 2	1.80	252 1	5 41
- 3		205 9	5 45
$Si(CH_3)_4$ - 1	1.90	398 3	7 04
- 2		341 0	7 08
- 3		313 1	7 10

TABLE 17

POTENTIAL ENERGY FUNCTION OF CF_4

Calculation	E^*, Å	E^*/k °K
CF_4 - 1	4.98	297.0
CF_4 - 2	4.94	271.2
CF_4 - 3	5.00	254.5

R/E^*	U/E^*	R/E^*	U/E^*
1.4877	-0.0957	1.1639	-0.4735
1.4611	-0.1078	1.1423	-0.5382
1.4346	-0.1217	1.1153	-0.6336
1.4080	-0.1378	1.0892	-0.7284
1.3814	-0.1564	1.0627	-0.8301
1.3549	-0.1780	1.0361	-0.9163
1.3283	-0.2032	1.0095	-0.9926
1.3017	-0.2325	0.9830	-0.9723
1.2752	-0.2656	0.9564	-0.7412
1.2486	-0.3070	0.9298	-0.0217
1.2220	-0.3540	0.9237	+0.2679
1.1955	-0.4092		

TABLE 16

POTENTIAL ENERGY FUNCTION OF C_2F_6

Calculation	R^*, A	ε^*/k, °K
C_2F_6 - 1	5 81	392 7
C_2F_6 - 2	5 825	352 2
C_2F_6 - 3	5 84	326 3

R/R^*	U/ε^*	R/R^*	U/ε^*
2 0258	-0 0099	1 4592	-0 0877
1 9742	-0 0117	1 4077	-0 1124
1 9227	-0 0139	1 3562	-0 1443
1 8712	-0 0166	1 3047	-0 1925
1 8197	-0 0199	1 2532	-0 2547
1 7682	-0 0240	1 2017	-0 3471
1 7167	-0 0292	1 1502	-0 4714
1 6652	-0 0358	1 0987	-0 6498
1 6137	-0 0442	1 0472	-0 8662
1 5622	-0 0550	0 9957	-0 9950
1 5107	-0 0691	0 9442	-0 2454

TABLE 19

POTENTIAL ENERGY FUNCTION OF CCl_4

Calculation	R^*, A	E^*/k
CCl_4 - 1	6.44	702.0
CCl_4 - 2	6.445	678.9
CCl_4 - 3	6.46	665.8

R/R^*	U/E^*	R/R^*	U/E^*
1.4534	-0.1043	1.1517	-0.5071
1.4260	-0.1186	1.1243	-0.5928
1.3985	-0.1339	1.0969	-0.6907
1.3711	-0.1508	1.0695	-0.7977
1.3437	-0.1777	1.0421	-0.9042
1.3163	-0.2046	1.0146	-0.9852
1.2889	-0.2364	0.9872	-0.9872
1.2614	-0.2739	0.9598	-0.7523
1.2340	-0.3164	0.9324	+0.0294
1.2066	-0.3711	0.9049	2.1619
1.1792	-0.4336		

TABLE 20

POTENTIAL ENERGY FUNCTION OF $C(CH_3)_4$

Calculation	R^*, A	E^*/k, °K
$C(CH_3)_4$ - 1	6 38	480 1
$C(CH_3)_4$ - 2	6 39	462 4
$C(CH_3)_4$ - 3	6 40	450 4

R/R^*	U/E^*	R/R^*	U/E^*
2 0376	-0 0142	1 4498	-0 1248
1 9984	-0 0160	1 4107	-0 1491
1 9592	-0 0181	1 3715	-0 1791
1 9201	-0 0206	1 3323	-0 2164
1 8809	-0 0235	1 2931	-0 2627
1 8417	-0 0268	1 2539	-0 3206
1 8025	-0 0307	1 2147	-0 3929
1 7633	-0 0354	1 1755	-0 4826
1 7241	-0 0408	1 1364	-0 5924
1 6850	-0 0473	1 0972	-0 7226
1 6458	-0 0550	1 0580	-0 8635
1 6066	-0 0642	1 0188	-0 9797
1 5674	-0 0753	0 9796	-0 9822
1 5282	-0 0887	0 9404	-0 8904
1 4890	-0 1049	0 9013	+1 3914

TABLE 21

POTENTIAL ENERGY FUNCTION OF $C_2(CH_3)_6$

Calculation	R^* A	E^*/k °K
$C_2(CH_3)_6$ - 1	7.14	715.6
$C_2(CH_3)_6$ - 2	7.16	683.4
$C_2(CH_3)_6$ - 3	7.17	651.8

R/R^*	U/E^*	R/R^*	U/E^*
2.0308	-0.0119	1.3305	-0.1929
1.9608	-0.0149	1.2605	-0.2788
1.8908	-0.0189	1.2255	-0.3377
1.8207	-0.0241	1.1905	-0.4106
1.7507	-0.0310	1.1555	-0.5006
1.6807	-0.0405	1.1204	-0.6099
1.6106	-0.0536	1.0854	-0.7380
1.5406	-0.0719	1.0504	-0.8749
1.4706	-0.0981	1.0154	-0.9342
1.4006	-0.1382	0.9804	-0.9550
		0.9454	-0.4821

TABLE 22

POTENTIAL ENERGY FUNCTION OF SF_6

Calculation SF_6 - 3

$R^* = 5.51$ Å

$E^*/k = 413.0$ °K

R/R^*	U/E^*	R/R^*	U/E^*
1.9944	-0.0120	1.3975	-0.1274
1.9419	-0.0143	1.3490	-0.1477
1.8875	-0.0172	1.2984	-0.1737
1.8330	-0.0208	1.2441	-0.2025
1.7786	-0.0253	1.1897	-0.2362
1.7241	-0.0311	1.1352	-0.2771
1.6697	-0.0384	1.0808	-0.3280
1.6152	-0.0478	1.0263	-0.3928
1.5608	-0.0601	0.9719	-0.4777
1.5064	-0.0764	0.9174	+2.3458
1.4519	-0.0981		

TABLE 23

POTENTIAL ENERGY FUNCTIONS OF SiF_4

SiF_4 - 1 $R^* = 5.37$ A $E^*/k = 344.2$ °K		SiF_4 - 2 $R^* = 5.41$ A $E^*/k = 252.1$ °K	
R/R^*	U/E^*	R/R^*	U/E^*
1.4571	-0.0881	2.0333	-0.0117
1.4418	-0.1039	1.9778	-0.0139
1.4246	-0.1232	1.9224	-0.0167
1.3873	-0.1468	1.8669	-0.0201
1.3501	-0.1759	1.8115	-0.0244
1.3128	-0.2120	1.7560	-0.0299
1.2756	-0.2569	1.7006	-0.0368
1.2384	-0.3132	1.6451	-0.0457
1.2011	-0.3835	1.5896	-0.0572
1.1639	-0.4723	1.5342	-0.0723
1.1266	-0.5820	1.4787	-0.0924
1.0894	-0.7138	1.4233	-0.1193
1.0521	-0.8598	1.3678	-0.1560
1.0149	-0.9816	1.3124	-0.2047
0.9777	-0.9450	1.2569	-0.2776
0.9590	-0.7520	1.2015	-0.3776
0.9404	-0.2959	1.1460	-0.5184
0.9218	+0.4590	1.0906	-0.7095
		1.0351	-0.9270
		0.9797	-0.9453
		0.9242	+0.4530

TABLE 24

POTENTIAL ENERGY FUNCTION OF $Si(CH_3)_4$ - 1

$R^* = 7.04$ Å

$\varepsilon^*/k = 360.3$ °K

R/R^*	U/ε^*	R/R^*	U/ε^*
0.9597	-0.0115	1.4560	-0.1083
1.0241	-0.0128	1.4205	-0.1277
1.9884	-0.0144	1.3849	-0.1512
1.9531	-0.0161	1.3494	-0.1800
1.9176	-0.0181	1.3139	-0.2153
1.8821	-0.0204	1.2784	-0.2588
1.8466	-0.0230	1.2429	-0.3127
1.8111	-0.0261	1.2074	-0.3795
1.7756	-0.0296	1.1719	-0.4621
1.7401	-0.0337	1.1364	-0.5633
1.7045	-0.0385	1.1009	-0.6860
1.6690	-0.0442	1.0653	-0.8195
1.6335	-0.0508	1.0298	-0.9475
1.5980	-0.0587	0.9943	-0.9965
1.5625	-0.0680	0.9588	-0.7539
1.5270	-0.0791	0.9233	+0.4142
1.4915	-0.0923		

TABLE 25

THERMAL PRESSURE COEFFICIENT AND COMPRESSIBILITY OF CF_4

Measurement	Observed $\Delta P/\Delta T_v$ atm /°K	α_v/β_{CF_4} atm /°K	$(\partial P/\partial T)_v$, atm /°K	$\beta \times 10^4$ atm $^{-1}$	Temperature °K
1	16.77	0.17	16.94	1.434	131.6
2	15.82	0.16	15.98	1.752	133.7
3	22.52	0.24	22.76	1.080	111.0
4	24.23	0.27	24.50	0.997	105.6
5	17.43	0.18	17.61	1.527	126.1
6	18.37	0.19	18.56	1.452	122.6
7	23.81	0.26	24.07	0.992	103.4
8	25.51	0.28	25.79	0.907	99.2
9	15.38	0.16	15.54	1.827	136.1
10	18.45	0.19	18.64	1.410	123.0
11	23.43	0.24	23.67	1.014	104.1
12	20.89	0.23	21.11	1.189	113.0
13	21.37	0.23	21.60	1.152	111.7
14	13.95	0.14	14.09	2.09	142.5
15	25.34	0.28	25.64	0.905	97.1

TABLE 24

THERMAL PRESSURE COEFFICIENT OF CH_4

Measurement	Observed $\Delta P/\Delta T$, atm /°K	α_c/β_{CH_4}, atm /°K	$(\partial P/\partial T)_V$ atm /°K	Temperature °K
1	14.64	0.14	14.78	105.6
2	15.67	0.15	15.82	102.7
3	15.06	0.14	15.19	105.4
4	15.40	0.15	15.55	104.2
5	14.90	0.14	15.04	108.0
6	15.04	0.14	15.18	108.0
7	16.00	0.16	16.16	99.7
8	16.69	0.17	16.86	93.7
9	16.50	0.16	16.66	100.3
10	18.28	0.16	18.44	94.0

TABLE 27

LIQUID MOLAR VOLUME CORRELATIONS AND EXTRAPOLATED LIQUID VOLUMES AT 0°K

Molecule	$A_1 \left[\frac{mole}{cc}\right]^2$	$B_1 \frac{mole^2}{cc^2 \times {}^\circ K}$	$V^\circ \frac{cc}{mole}$	From Molar Volumes R°	Empirical R°_{6-12}	Calculated in Part I R°
A	2.2231×10^{-3}	1.1360×10^{-5}	21.21	3.68	3.84	----
N_2	1.5540×10^{-3}	9.3777×10^{-6}	25.36	3.91	4.15	3.61
O_2	2.2903×10^{-3}	1.1284×10^{-5}	20.09	3.66	3.92	3.70
F_2	2.0154×10^{-3}	1.4536×10^{-5}	18.85	3.54	3.71	3.86
CH_4	1.2234×10^{-3}	4.702×10^{-6}	28.59	4.07	4.32	----
C_2H_6	6.147×10^{-4}	1.5467×10^{-5}	40.33	4.56	4.97	5.44
CF_4	6.302×10^{-4}	2.0159×10^{-6}	39.83	4.54	5.28	4.99
CCl_4	1.8365×10^{-4}	2.597×10^{-7}	73.79	5.58	6.60	6.44
$C(CH_3)_4$	1.4289×10^{-4}	2.585×10^{-7}	83.66	5.82	6.25	6.36

TABLE 28

x FOR CH_4 AND CF_4

CF_4		CH_4	
Temperature, °K	x	Temperature °K	
131.6	1.025	105.6	0.772
133.7	0.996	102.7	0.788
111.0	1.030	105.4	0.791
105.6	1.030	104.2	0.794
126.1	0.985	108.0	0.816
122.6	0.990	108.0	0.825
103.4	0.980	99.7	0.804
99.2	0.990	95.7	0.837
134.1	1.002	100.3	0.799
128.0	1.000	94.0	0.823
104.1	0.976		
113.0	0.985		
111.7	0.990		
142.5	0.998		
97.1	0.961		

TABLE 29

CONFIGURATIONAL ENERGIES AND MOLAR VOLUMES OF LIQUIDS

CF_4			C_2H_6		
T, °K	E_c cal/mole	V, cc/mole	T, °K	E_c cal/mole	V cc/mole
100	-3005	48 80	90	-4136	45 85
110	-2941	49 48	100	-4028	46 79
120	-2844	50 75	110	-3921	47 72
122	-2847	51 01	120	-3815	48 66
130	-2771	52 12	130	-3715	49 61
140	-2640	53 61	140	-3618	50 55
145 2	-2595	54 43	150	-3521	51 52
150	-2527	55 23	160	-3426	52 49
	C_2F_6		170	-3331	53 49
			180	-3233	54 53
194 9	-3537	85 9	190	-3131	55 63
194 9	-3482	65 9	200	-3037	56 83
	$C(CH_3)_4$		210	-2941	58 17
			220	-2845	59 65
282 66	-5206	119 6	230	-2747	61 40
298 16	-4744	123 31	240	-2646	63 36
			250	-2542	65 62
			260	-2433	68 31
			270	-2317	71 61
			280	-2190	75 85
			290	-2044	82 49
			300	-1783	95 09

TABLE 30

PARAMETERS USED IN FIGURES 43 AND 44

Experimental 6-12 Potential Parameters

Substance	ε/k, °K	σ, Å	Source
A	120	3.84	1
N_2	94.1	4.15	1
O_2	116	3.92	1
CH_4	144	4.32	1
C_2H_6	224	5.045	This work
CF_4	146.8	5.24	21,43
C_2F_6	163	6.24	21
CCl_4	327	6.60	1
$C(CH_3)_4$	236	6.25	21

Calculated Parameters

N_2	129.4	3.61
O_2	152.6	3.70
C_2H_6	275	5.045
CF_4	271.2	4.99
C_2F_6	352.2	5.825
CCl_4	678.9	6.445
$C(CH_3)_4$	480.1	6.38

TABLE A1

RELATIONSHIP BETWEEN x_0^* AND r^*/ℓ

	r^*/ℓ	E^*/ℓ
4.245	7.763	8.49
3.290	5.655	6.58
3.065	5.149	6.13
2.735	4.387	5.47
2.515	3.863	5.03
3.275	5.41	6.55
1.900	2.35	3.80
1.68	1.78	3.36
1.83	2.17	3.66
1.75	1.98	3.50
1.76	1.99	3.52
2.08	2.90	4.16
1.865	2.24	3.730
1.853	2.23	3.706

TABLE A2

SPHERICAL SHELL POTENTIAL

$r_0^* = 1.70$

$r^*/a = 1.85$

r^*	U/ε^*	R/R^*	U/ε^*
0.000	-0.0109	1.411[illegible]	-0.1130
1.9412	-0.0132	1.3529	-0.1525
1.8824	-0.0161	1.2941	-0.2095
1.8235	-0.0199	1.2353	-0.2927
1.7647	-0.0247	1.1765	-0.4155
1.7059	-0.0310	1.1176	-0.5947
1.6471	-0.0392	1.0588	-0.8330
1.5882	-0.0501	1.0000	-1.0000
1.5294	-0.0648	0.9412	-0.9368
1.4706	-0.0850	0.8824	-0.9354

TABLE - 3

SPHERICAL SHELL POTENTIAL

$r_a^* = 1.80$

$r^*/\rho = 2.10$

[illegible]	U/E^∞	R/R^*	[illegible]
9.00	-0.0123	1.3889	[illegible]
9.144	-0.0147	1.3333	[illegible]
8889	-0.0177	1.2778	[illegible]
1.3333	-0.0215	1.2222	-0.1337
1.7778	-0.0263	1.1667	-0.2595
1.7222	-0.0324	1.1111	-0.4039
1.5667	-0.0402	1.0556	-0.5518
1.6111	-0.0503	1.0000	-1.0000
1.5556	-0.0637	0.9444	-0.3704
1.5000	-0.0814	0.8889	+0.2946
1.4444	-0.1051		

TABLE A1

SPHERICAL SHELL POTENTIAL

$r_0^* = 1.90$

$r^*/\ell = 2.35$

	U/E^*		R/R^*	
1.990	-0.014		1.331	-0.1[illegible]
1.930	-0.017		1.279	-0.265
1.870	-0.021		1.213	-0.367
1.810	-0.026		1.153	-0.512
1.750	-0.032		1.094	-0.730
1.690	-0.040		1.03	-0.933
1.630	-0.051		0.975	-0.975
1.570	-0.065		0.935	-0.878
1.510	-0.084		1.010	-0.982
1.450	-0.109		0.935	-0.898
1.391	-0.145		0.935	-0.190

SPHERICAL SHELL POTENTIAL

$$r_0^* = 2.00$$

$$r^*/\rho = 2.61$$

R/R*	U/E*	R/R*	
2.0000	-0.0150	1.4000	[illegible]
1.9500	-0.0174	1.3500	[illegible]
1.9000	-0.0203	1.3000	[illegible]
1.8500	-0.0236	1.2500	[illegible]
1.8000	-0.0293	1.2000	[illegible]
1.7500	-0.0352	1.1500	-0.3434
1.7000	-0.0424	1.1000	-0.4092
1.6500	-0.0514	1.0500	-0.4924
1.6000	-0.0628	1.0000	-0.5930
1.5500	-0.0773	0.9500	-0.7166
1.5000	-0.0958	0.9000	-0.8725
1.4500	-0.1197		

TABLE A6

SPHERICAL SHELL POTENTIAL

$r_0^* = 2.10$

$r^*/\rho = 2.86$

	U/E^*		r/R^*	U/E^*
1.0000	-0.0162		1.4286	-0.1345
1.0524	-0.0188		1.3810	-0.1740
1.0048	-0.0220		1.3333	-0.2187
1.0571	-0.0258		1.2857	-0.2770
1.0095	-0.0304		1.2381	-0.3532
1.0619	-0.0361		1.1905	-0.4527
1.1143	-0.0430		1.1429	-0.5804
1.1667	-0.0515		1.0952	-0.7377
1.2190	-0.0620		1.0476	-0.9059
1.2714	-0.0752		1.0000	-1.0000
1.3238	-0.0917		0.9524	-0.7004
1.3762	-0.1127		0.9048	+1.1666

SPHERICAL SHELL POTENTIAL

$$r_o^* = 2\ 20$$

$$r^*/\rho = 3\ 11$$

r*/r*	U/E*	R/R*	U/E*
2 0000	-0 0173	1 5091	-0 1602
1 9545	-0 0200	1 3636	-0 1978
1 9091	-0 0231	1 3182	-0 2458
1 8636	-0 0269	1 2727	-0 3076
1 8182	-0 0315	1 2273	-0 3865
1 7727	-0 0369	1 1818	-0 4874
1 7273	-0 0435	1 1364	-0 6139
1 6818	-0 0516	1 0909	-0 7741
1 6364	-0 0614	1 0455	-0 9767
1 5909	-0 0735	1 0000	-1 0000
1 5454	-0 0885	0 9545	-0 7480
1 5000	-0 1072	0 9091	+0 6953
1 4545	-0 1306		

TABLE A8

REDUCED BOYLE TEMPERATURE FOR THE SPHERICAL SHELL POTENTIAL

r_0^*	T_B^*
1.2	0.725
1.3	0.943
1.4	1.137
1.5	1.311
1.6	1.468
1.7	1.608
1.8	1.735
1.9	1.850
2.0	1.953
2.5	2.355
3.0	2.612
3.5	2.795
4.0	2.922
∞	3.420

APPENDIX

LENNARD-JONES 6-12 POTENTIAL

U/ε^*	r/r^*	U/ε^*
-0.0310	1.40	-0.2459
-0.0360	1.35	-0.3031
-0.0421	1.30	-0.3714
-0.0493	1.25	-0.4556
-0.0579	1.20	-0.5576
-0.0684	1.15	-0.6777
-0.0811	1.10	-0.8103
-0.0967	1.05	-0.9554
-0.1157	1.00	-1.0000
-0.1390	0.95	-0.9701
-0.1679	0.90	-0.8224
-0.2034	0.85	+1.7273

TABLE B2

[illegible]-JONES 6-14 POTENTIAL

[illegible]	[illegible]	r/r^*	U/ε^*
[illegible]	[illegible]	1 40	-0 2267
[illegible]	[illegible]	1 35	-0 2779
1 90	[illegible]	1 30	-0 3435
1 85	[illegible]	1 25	-0 4258
1 80	[illegible]	1 20	-0 5277
1 75	[illegible]	1 15	-0 6506
1 70	[illegible]	1 10	-0 7903
1 65	[illegible]	1 05	-0 9271
1 60	[illegible]	1 00	-1 0000
1 55	[illegible]	0 95	-0 8427
1 50	[illegible]	0 90	-0 0145
1 45	[illegible]	0 85	+2 6578

TABLE B3

LENNARD-JONES 6-14 POTENTIAL

r/r*	U/ε*	r/r*	U/ε*
1.80	-0.02499	1.20	[illegible]
1.90	+0.03400	1.10	[illegible]
1.80	+0.04699	1.00	[illegible]
1.70	-0.06617	0.975	-0.943
1.60	-0.09303	0.950	-0.6132
1.50	-0.13955	0.925	-0.4455
1.40	-0.20797	0.900	-0.2276
1.30	-0.3225		

TABLE B4

LENNARD-JONES 6-12 POTENTIAL

r/σ	U/ε^*	r/r^*	U/ε^*
1.00	-0.0234	1.40	-0.1980
1.05	-0.0273	1.35	-0.2455
1.10	-0.0319	1.30	-0.3063
1.15	-0.0374	1.25	-0.3842
1.20	-0.0441	1.20	-0.4836
1.25	-0.0522	1.15	-0.6081
1.30	-0.0621	1.10	-0.7646
1.35	-0.0743	1.05	-0.9116
1.40	-0.0893	1.00	-1.0000
1.45	-0.1080	0.95	-0.7816
1.50	-0.1313	0.90	+0.5087
1.55	-0.1608		

TABLE B5

LENNARD-JONES 6-20 POTENTIAL

r*	U/ε
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
1.0	[illegible]
0.975	-0.9959
0.950	-0.7479
0.925	-0.2427

TABLE 55

[illegible] JONES 7-14 POTENTIAL

[illegible]	[illegible]	r/r^*	U/ε^*
2.00	-0.0156	1.40	-0.1807
1.95	-0.0186	1.35	-0.2258
1.90	-0.0222	1.30	-0.2933
1.85	-0.0268	1.25	-0.3754
1.80	-0.0324	1.20	-0.4803
1.75	-0.0391	1.15	-0.6105
1.70	-0.0481	1.10	-0.7830
1.65	-0.0592	1.05	-0.9143
1.60	-0.0731	1.00	-1.0000
1.55	-0.0909	0.95	-0.8134
1.50	-0.1136	0.90	+0.1697
1.45	-0.1429		

	-0.0559		
	-3.0597		
	-3.0878		43
			80
		5	00
	-3. 67	940	3
	-0.0 3.00	0.925	3
	-0.0 4073	0.940	5
	-0.0 5373		

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	1.40	[illegible]
[illegible]	[illegible]	1.35	[illegible]
[illegible]	[illegible]	1.30	[illegible]
[illegible]	[illegible]	1.25	[illegible]
[illegible]	[illegible]	1.20	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	0.95	[illegible]
[illegible]	[illegible]	0.90	[illegible]

APPENDIX C

THERMAL PRESSURE COEFFICIENT

Present		Measurements	
Temperature °C	Gage Pressure psi	Temperature °C	Gage Pressure psi
-1 21	93	0 33	34
-1 [illegible]	110	0 34	38
- [illegible]	181	0 47	5[illegible]
- [illegible]	224	0 56	62
- 17	265	0 75	88
- 10	279	0 77	[illegible]5
-1 03	290	0 [illegible]	[illegible]0
-0 95	306	1 06	157
-0 85	322	0 95	1[illegible]8
-0 73	347	0 92	128
-0 60	371	1 09	155
-0 [illegible]6	396	1 24	18[illegible]
-0 38	420	1 [illegible]3	2[illegible]3
-0 17	450	1 45	227 5
+0 04	499	1 54	7[illegible]0
0 17	527	1 65	2[illegible]
0 43	575	1 79	[illegible]0
0 73	633	2 06	[illegible]
0 [illegible]6	657	2 21	37[illegible]
1 06	698	2 37	[illegible]5
		2 45	427
		2 60	447
		2 77	478
		2 90	500
		3 05	524

...AL PRESSURE COEFFICIENT OF CF_4

		Measurement 1	
...ature	...sure psi	Thermocouple M-1 e.m.f. mv	Gage Pressure psi
	311	49	-4.3846	44
	868	75	-4.3811	76
	958	0	-4.3778	107
	714	98	-4.3736	149
	-9	6	-4.3711	173
	1 0	23	-4.3668	224
	071	0.7	-4.3588	284
	654	30[illegible]	-4.3568	316
	394b	14[illegible]	-4.3510	377.5
	0894	9[illegible]3	-4.3403	486
	8853	5[illegible]	-4.3415	469
	807	60[illegible]	-4.3397	489
	8[illegible]8	3[illegible]6	-4.335[illegible]	538
	811	9[illegible]2	-4.3331	556
	8309	1135	-4.3296	597
			-4.3221	669
			-4.3176	715
			-4.3126	762.5
			-4.3077	812
			-4.3035	852
			-4.2945	940
			-4.2910	982.2
			-4.2863	1027

TABLE C3

[illegible]AL PRESSURE CARTRIDGE OF CF_4

Measurement 3		Measurement 4	
Thermocouple K-1 e.m.f. mv	Gage Pressure psi	Thermocouple K-1 e.m.f. mv	Gage Pressure psi
-4.9798	49	-4.9914	81
-4.9745	127	-4.9870	100
-4.9724	153	-4.9849	148
-4.9662	248	-4.9812	240
-4.9622	315	-4.9765	280
-4.9586	373	-4.9735	345
-4.9564	408	-4.9703	398
-4.9551	432.5	-4.9672	454
-4.9476	546	-4.9638	512.5
-4.9449	586	-4.9606	568
-4.9424	630	-4.9571	627
-4.9392	680	-4.9522	720
-4.9355	727.5	-4.9490	778
-4.9337	777	-4.9437	875
-4.9307	831		
-4.9283	882.5		
-4.9259	896		
-4.9239	932.5		
-4.9211	970		

TABLE C4

PRESSURE COEFFICIENTS

			50
			75
			100
			24
	316		59
	345		
	322		
	1796		
	10		
	175		
	5143		
	5096		
	5026		
	73		787
	827		902
	4875		1000
-4	4811		
-4	4743		
-4	4665		

TABLE

[illegible] ASSURE CONTAINING [illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	275	[illegible]
[illegible]	325	[illegible]
[illegible]	375	[illegible]
[illegible]	425	[illegible]
[illegible]	475	[illegible]
[illegible]	525	[illegible]
[illegible]	575	[illegible]
[illegible]	630	[illegible]

TABLE C6

PRESSURE COEFFICIENT OF CF_4

		Measurement 10	
	ss re	Thermocouple ..-1 e m f mv	Gage Pressure psi
	222	-4.620	50
	44	-4.670	100
	7	-4.690	150
	832	-4.8 ..	200
	987	-4.900	250
	2044	-4.937	300
	2093	-4.960	350
	2339	-4.9 ..	400
	2	-5.026	500
	735	-5.0..	551
	986	-5.094	600
	3083	-5.7	650
		-5.99	7..5
		-6..	800
		-6.177	874
		-6.551	9.0
	2374	-6..	1026
	2324		
	2276		

| | | |

...L PRESSURE COEFFICI...

...	Gage Pressure, psi	Thermocouple ...-1 mv	Gage ... psi
... 371	149	-... 1753	
... 4320	226	-... 1675	9
... 0747	302	-... 1610	...
... 0...	387	-... 1553	200
... 8339	496	-... 1491	252
... 8279	597	-... 1435	300
... 8208	710	-... 1375	349
... 8145	800	-... ...	403
... 8074	9...	-... 2...	456
... 7990	102...	-... ...	5...
		-... 12	570
		-... 10...	6...
...		-... 09...	717 5
...		-... 07...	795
...		-... 0744	889
...	...		
...	...		
...	565		
...	...		
...	...		
...	...		
...	...		

THERMAL PRESSURE COEFFIC

[illegible]	Measurement 1	Measurement 2	
[illegible]	Gage Pressure psi	Thermocouple E.M.F.	Gage Pressure psi
[illegible]	280	-5.0 7	76
[illegible]55	324	-3.0	149
[illegible]66	387	-3.0	223
[illegible]880	77	-2.0235	302
[illegible]923	542	-1.0	380
[illegible]922	622	-1.0	456
[illegible]464	723	-0.0	541
[illegible]5048	828	-0.0	629
[illegible]6949	924	-0.0	723
	10.9	-0.0235	831
		-0.0	928
		-0.0624	1022.5

TABLE C10

THERMAL PRESSURE COEFFICIENT OF CH_4

Measurement 3		Measurement 4	
Thermocouple M-1 e m f, mv	Gage Pressure, psi	Thermocouple M-1 e m f, mv	Gage Pressure psi
-4.9701	75	-5.0175	50
-4.9836	147.5	-5.0038	147.5
-4.9764	220	-5.0017	223
-4.9692	302	-4.9944	300
-4.9615	384	-4.9878	375
-4.9542	465	-4.9816	448
-4.9440	577.5	-4.9753	519
-4.9352	672	-4.9684	598
-4.9265	771	-4.9433	876
-4.9165	879	-4.9265	955
-4.9050	1008.5	-4.9290	1045

TABLE C11

THERMAL PRESSURE COEFFICIENT OF CH_4

Measurement 5		Measurement 6	
[illegible]-1	Gage Pressure, psi	Thermocouple M-1 e.m.f. mv	Gage Pressure, psi
[illegible]8559	398	-4.9366	75
[illegible]8997	479	-4.9301	150
[illegible]8938	549	-4.9224	227
[illegible]8853	625	-4.9158	301
[illegible]8769	705	-4.9093	375
[illegible]8697	799	-4.9025	450
[illegible]8606	900	-4.8953	525
[illegible]8509	1000	-4.8884	599
		-4.8810	675
		-4.8744	749
		-4.8676	824
		-4.8606	899
		-4.8517	974

TABLE C12

THERMAL PRESSURE COEFFICIENT OF CH_4

Measurement 7		Measurement 8	
Thermocouple M-1 e m f mv	Gage Pressure psi	Thermocouple M-1 e m f mv	Gage Pressure psi
-5.1105	25	-5.1702	286
-5.1043	100	-5.1648	362
-5.0955	201	-5.1590	439
-5.0893	277	-5.1530	525
-5.0832	351	-5.1470	614
-5.0775	424	-5.1405	701
-5.0714	499	-5.1345	789
-5.0649	584	-5.1284	874
-5.0579	672	-5.1213	973
-5.0505	742.5		
-5.0436	848		
-5.0371	937		
-5.0293	1026		

TABLE C13

[redacted]RAL PRESSURE COEFFICIENT OF CH_4

Measurement 9		Measurement 10	
Thermocouple M-1 e m f , mv	Gage Pressure, psi	Thermocouple M-1 e m f mv	Gage Pressure psi
-5 0982	6	-5 1484	258
-5 0916	91	-5 1584	347 5
-5 0858	150	-5 1623	433
-5 04?%	599	-5 1471	503
-5 0430	683	-5 1418	503
-5 0356	769	-5 1353	672 5
-5 0274	875	-5 1291	757
-5 01?%	960	-5 1244	838
-5 0140	1036	-5 1170	902
		-5 1100	1013

NOMENCLATURE

[illegible]	Number of atoms of type A in a molecule
[illegible]	Reduced van der Waals' a
[illegible]	Constant in molar volume correlation equation 16; [illegible] in Part II Defined by Equation 40
[illegible]	Number of atoms of type B in a molecule
[illegible]	Second virial coefficient also sometimes written as just B Used in Part I and defined by Equation 12
[illegible]	Constant in molar volume correlation for liquids in Part II Defined by Equation 40
$B^*(T^*)$	Reduced second virial coefficient also written as just B^*
C	Number of atoms of type C in a molecule Also a parameter defined by Equation 17 and used only in Equations 14-19
C'(T)	Third virial coefficient, used in Part I and defined by Equation 12
[illegible]	Geometrical constant in cell model to account for non-nearest neighbor interactions used in Part II
[illegible]	Part I Number of atoms of type D in a molecule Also a parameter defined by Equation 18 and used only in Equations 14-19 Part II Average distance between molecular centers in a liquid
[illegible]	Fourth virial coefficient used in Part I and defined by Equation 12
[illegible]	Geometrical constant in cell model to account for non-nearest neighbor interactions used in Part II
[illegible]	e.m.f. of thermocouple
[illegible]	Configurational energy

	Value of -U(R) at the minimum in U(R) Used as an energy parameter for a molecule
g(R V,T)	Radial distribution function also written as g(R) and $\phi_1(y\ V/R^3\ T^*)$
k	Boltzmann's constant
m	Attractive constant in the general form of the Lennard-Jones potential
	Repulsive constant in the general form of the Lennard-Jones potential
N	Number of molecules usually taken as Avogadro's Number
	Average number of molecules per unit volume
P	Pressure
P_c	Critical pressure
r	Part I Distance between centers of atoms or molecules Part II Distance of a molecule from the center of its cell
r_0	Value of r when U(r) = 0 Usually used as a parameter for an atom
r_m	Value of r at the minimum of U(r) Usually used as a parameter for an atom
R	Spherical shell potential parameter that accounts for shape of reduced potential energy function
	Distance between molecular centers Used as gas constant only in Equations 12, 31 and 31
R_0	Value of R when U(R) = 0 Used as a parameter for a molecule
R_m	Value of R at the minimum in U(R) Used as a parameter for a molecule
	R^*/R_0
T	Temperature, °C
	Absolute temperature
T^*	Reduced temperature kT/E^*
T_b	Boyle temperature

	temperature, kT_B/E^*
	temperature
	temperature T/T_c
	potential energy of interaction between nonadjacent molecules of different molecules
	pair potential energy function for an isolated pair of atoms or molecules $U(R)$ is for a pair of molecules
	Portion of potential energy function defined by Equation 55
	Volume per molecule
	Volume per molecule when the average separation between molecules is R^*
	Volume of sample cell or molar volume
	Molar volume at 0°K
	Molar volume when the average separation between molecules is R^*
	Potential energy of interaction of a molecule in a cell with its neighbors
	Potential energy when all molecules are at the centers of their cells
	Defined by Equation 53
	Part I Variable defined by Equation 16 and used only in Equations 14-27 Part II $y = R/R^*$
	Number of nearest neighbors to a molecule in its cell
α	Part I Variable defined by Equation 10 Part II Cubical coefficient of thermal expansion
α_e	Cubical coefficient of thermal expansion of sample cell in experimental apparatus
β	Part I Variable defined by Equation 11 Part II Compressibility
β_c	Compressibility of material of construction of sample cell in experimental apparatus

	Parameter defined by Equation 9
	Gamma function
	Value of -U(r) at the minimum is U(r) Usually used as a parameter for atoms
ρ	Distance from the center of a molecule to the center of a constituent atom
τ	Volume
ω	Acentric factor is Pitzer's correlation (10)

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